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**NUCLEAR SCIENCE SERIES**

# **The Radiochemistry of Ruthenium**

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# The Radiochemistry of Ruthenium

E. I. WYATT and R. R. RICKARD

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Subcommittee on Radiochemistry  
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## FOREWORD

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences - National Research Council. Its members represent government, industrial, and university laboratories in the areas of nuclear chemistry and analytical chemistry

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the establishment of specifications for radiochemically pure reagents, availability of cyclotron time for service irradiations, the place of radiochemistry in the undergraduate college program, etc.

This series of monographs has grown out of the need for up-to-date compilations of radiochemical information and procedures. The Subcommittee has endeavored to present a series which will be of maximum use to the working scientist and which contains the latest available information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or a group of closely related elements.

An expert in the radiochemistry of the particular element has written the monograph, following a standard format developed by the Subcommittee. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to the radiochemist but also to the research worker in other fields such as physics, biochemistry or medicine who wishes to use radiochemical techniques to solve a specific problem.

W. Wayne Meinke, Chairman  
Subcommittee on Radiochemistry

## INTRODUCTION

This volume which deals with the radiochemistry of ruthenium is one of a series of monographs on radiochemistry of the elements. There is included a review of the nuclear and chemical features of particular interest to the radiochemist, a discussion of problems of dissolution of a sample and counting techniques, and finally, a collection of radiochemical procedures for the element as found in the literature.

The series of monographs will cover all elements for which radiochemical procedures are pertinent. Plans include revision of the monograph periodically as new techniques and procedures warrant. The reader is therefore encouraged to call to the attention of the author any published or unpublished material on the radiochemistry of ruthenium which might be included in a revised version of the monograph.

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# The Radiochemistry of Ruthenium

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## 2. Radioisotopes of Ruthenium

The radioisotopes of ruthenium are listed in Table 2.1. The values for half lives and radiation energies are those that appear first in the lists by Strominger, Hollander, and Seaborg.<sup>(49)</sup> Additional information about ruthenium radioisotopes, including references to the original literature, is given by Strominger, Hollander, and Seaborg.<sup>(49)</sup>

Table 2.1. Radioisotopes of Ruthenium

<u>Radioisotope</u>	<u>Half Life</u>	<u>Type of Decay</u>	<u>Radiations</u>	
			<u>Type</u>	<u>Energies, Mev</u>
Ru <sup>93</sup>	50 s	$\beta^+$	--	----
Ru <sup>94</sup>	~57 m	EC	--	----
Ru <sup>95</sup>	1.65 h	EC, $\beta^+$	$\beta^+$	1.1
			$\gamma$	0.145, 0.340, 0.640, 1.11
Ru <sup>97</sup>	2.88 d	EC	$\gamma$	0.109, 0.216, 0.325, 0.570
Ru <sup>103</sup>	39.8 d	$\beta^-$	$\beta^-$	0.119, 0.227
			$\gamma$	0.055, 0.297, 0.323, 0.366, 0.498, 0.610
Ru <sup>105</sup>	4.5 h	$\beta^-$	$\beta^-$	1.150
			$\gamma$	0.726
Ru <sup>106</sup>	1.00 y	$\beta^-$	$\beta^-$	0.0392
Ru <sup>107</sup>	4 m	$\beta^-$	$\beta^-$	~4
Ru <sup>108</sup>	~4 m	$\beta^-$	--	----

Since rutheruthenium became available, the radiochemist has been better able to understand the various complex reactions of ruthenium. Adequate methods for the preparation of ruthenium tracer have been reported, <sup>(24,36)</sup> but the results of many studies made with tracers are open to question because of isotope-exchange effects.

### 3. Ruthenium Chemistry of Interest to Radiochemists

#### 3.1 Ruthenium Metal

Ruthenium belongs to Subgroup VIII, Platinum Metals. In radiochemical processes, ruthenium may be present as ruthenium(II), -(III), -(IV), -(VI), -(VII), or -(VIII). Ruthenium(V) exists but is unlikely to be encountered. Ruthenium is infamous in its chemical behavior because of its many valence states.

The pure metal resembles platinum in color and lustre but is dull gray when finely divided. The amorphous form may appear black. The most satisfactory way of determining ruthenium is by reduction to the metal. In conventional chemical analyses the oxidized ruthenium is reduced by ignition in hydrogen. In radiochemistry the reduction is effected with powdered magnesium metal. Like the other platinum metals, ruthenium readily occludes gases; it unites with oxygen more readily than do any of the group except osmium. The formation of ruthenium sulfides, tellurides, and selenides has been reported. <sup>(20)</sup>

The metal is usually dissolved by means of alkali-metal nitrate—peroxide fusion; acids and mixtures of acids have little dissolution effect. The fluorination or chlorination of ruthenium at high temperatures yields various soluble fluorides or chlorides of ruthenium. Similar reactions have been noted for the other platinum metals, particularly osmium. Black noncrystalline ruthenium dissolves readily in an alkaline solution of sodium hypochlorite or potassium periodate.

Ruthenium alloys should be dissolved with caution. Ruthenium-uranium alloys have been dissolved safely in a 4:1 mixture of hydrochloric

and nitric acids, whereas ruthenium-zinc alloys have been observed to explode violently in the presence of hydrochloric acid.<sup>(23)</sup>

There is little commercial use for ruthenium metal because it is brittle and oxidizes easily. Some of the physical and chemical properties of ruthenium are given in Table 3.1.

Table 3.1. Some Physical and Chemical Properties of Ruthenium<sup>(\*)</sup>

Atomic weight	- - -	101.1
Atomic number	- - -	44
Period	- - - - -	Group VIII, transition series Ru, Rh, Pd
Color	- - - - -	Gray-white; black (amorphous)
Specific gravity	-	12.2 (gray); 8.6 (black)
Melting point	- - -	2500°C (gray)
Boiling point	- - -	4110°C (gray)
Alloys	- - - - -	With Ir, Cu, Ag, Au, W, Sn, Pb, Fe, Co, Ni, U

### 3.2 Compounds of Ruthenium

Ruthenium is analogous to the transition elements cobalt, iron, and nickel in its formation of numerous coordination complexes with the ligands, O, Cl, NO, NO<sub>2</sub>, NO<sub>3</sub>, OH, OH<sub>2</sub>, CN, SCN, etc.

3.2.1 Oxides. The oxides of ruthenium that are encountered most often in radiochemistry are the tetroxide, RuO<sub>4</sub>, and the dioxide, RuO<sub>2</sub>. The tetroxide is formed in acid solutions by strong oxidants. It has been isolated, and its chemical and physical properties have been determined.<sup>(47)</sup> Ruthenium tetroxide melts at about 26°C and begins to volatilize at 45°C; the volatilization is nearly complete at 110°C. The volatility

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\* Data taken from N. A. Lange, Handbook of Chemistry, 9th ed., p. 298, 1956 and from J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. XV, p. 510, Longmans, Green, New York, 1942.

of the tetroxide<sup>(17)</sup> has been used extensively in radiochemistry. Ruthenium can be decontaminated from the other fission products by distillation as ruthenium tetroxide, especially if perchloric acid is the oxidizing agent. The high boiling point of  $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$  ( $200^\circ\text{C}$ ) ensures the complete distillation of ruthenium tetroxide.<sup>(19)</sup> Halogens that distil under these conditions can be oxidized to their nonvolatile oxyacids by the addition of sodium bismuthate before the distillation is made.<sup>(19)</sup> Technetium, in combination, distills but can be separated from ruthenium by precipitating the ruthenium with ethyl alcohol in a solution of sodium hydroxide. Molybdenum can be rendered nonvolatile by the addition of phosphoric acid.<sup>(19)</sup> Ruthenium tetroxide is easily reduced by the mildest reducing agents, and in some cases it decomposes violently; it is stable only in acid solutions and in halogenated organic solvents. Radiochemists have made use of the solubility of the tetroxide in carbon tetrachloride in separation schemes.<sup>(33)</sup> The results of distribution studies are given in Tables 3.2 and 3.3 and in Fig. 3.1. When ruthenium tetroxide is trapped in caustic solution, the ruthenates and perruthenates, which are formed immediately, slowly decompose to the dioxide.<sup>(47)</sup>

Table 3.2. Distribution of Ruthenium Tetroxide between Carbon Tetrachloride and Water at  $20^\circ\text{C}$  (\*)

<u><math>\text{RuO}_4</math> in <math>\text{CCl}_4</math> Phase (A), <math>\text{M} \times 10^2</math></u>	<u><math>\text{RuO}_4</math> in <math>\text{H}_2\text{O}</math> Phase (B), <math>\text{M} \times 10^4</math></u>	<u><math>D = A/B</math></u>
0.569	0.964	59.0
3.80	6.30	60.5
5.25	9.00	58.4
5.56	9.70	57.4
5.60	9.60	58.2
6.63	11.5	57.6
11.9	20.5	58.1

\* Data taken from Table 1 of F. S. Martin, J. Chem. Soc., 2565 (1954), with permission of the author and The Chemical Society.

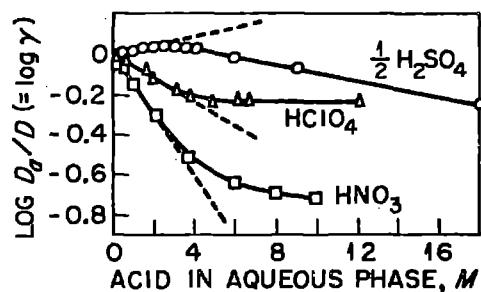


Fig. 3.1. Distribution of  $\text{RuO}_4$  between  $\text{CCl}_4$  and Aqueous Acids.  
[Reproduced from Fig. 2 of F. S. Martin, J. Chem. Soc., 2566 (1954), with permission of the author and The Chemical Society.]

Table 3.3. Distribution of Ruthenium Tetroxide between Carbon Tetrachloride and Sodium Hydroxide Solution at  $20^\circ\text{C}^{(*)}$

NaOH in $\text{H}_2\text{O}$ Phase, $\text{M} \times 10^3$	$\text{RuO}_4$ in $\text{CCl}_4$ Phase (A), $\text{M}$	$\text{RuO}_4$ in $\text{H}_2\text{O}$ Phase (B), $\text{M} \times 10^3$	$D = A/B$	$10^{12}K_a^{(**)}$
0.943	0.128	3.59	35.6	6.7
0.943	0.120	3.42	35.1	6.9
0.943	0.0427	1.19	36.0	6.5
1.886	0.435	1.72	25.3	6.8
1.886	0.377	1.51	25.0	7.0
9.43	0.0287	3.64	7.9	6.7

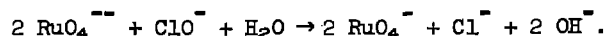
Ruthenium dioxide, in contrast to the tetroxide, behaves similarly to manganese dioxide. The refractory form is obtained by either thermal destruction of ruthenium salts or oxidation of the metal in oxygen.<sup>(29)</sup> The usual radiochemical form of the dioxide is the hydrous oxide,  $\text{RuO}(\text{OH})_2$ ,<sup>(47)</sup> which is readily soluble in warm hydrochloric acid but is less soluble in nitric acid and in sulfuric acid. The hydrous oxide

\* Data taken from Table 2 of F. S. Martin, J. Chem. Soc., 2566 (1954), with permission of the author and The Chemical Society.

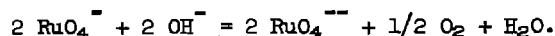
\*\*  $K_a$  = acid dissociation constant.

is formed by the addition of a base to a compound of ruthenium(IV) or by either the reduction with mild reductants (such as ethyl alcohol) or the autoreduction of perruthenates and ruthenates.

3.2.2 Perruthenates and Ruthenates. Perruthenates,  $M_1(RuO_4)$ , are formed by the reduction of ruthenium tetroxide in alkaline solution or by the oxidation of a lower-valent species of ruthenium in alkaline solution by hypochlorite or periodate, as indicated by the equation<sup>(9)</sup>



In alkaline solutions that contain an oxidizing agent, ruthenium(VI) is oxidized to ruthenium(VII), and, if an excess of oxidizing agent is present, some ruthenium(VIII) is formed. Ruthenium(VII) is at the same time reduced by the hydroxide ion to ruthenium(VI) according to the equation<sup>(9)</sup>



Therefore ruthenium may exist simultaneously in all three valence states in various proportions depending on the basicity, the amount of oxidant, and the presence or absence of catalysts.

The perruthenates are not stable in acid solution; they decompose to form lower-valent ruthenium compounds. Acids of composition corresponding to the hypothetical formulas  $H_2RuO_4$  and  $HRuO_4$  have not been found to exist. Acidification of the perruthenate form usually yields ruthenium tetroxide and ruthenium(IV).

Ruthenates,  $M_2(RuO_4)$ , are presumed to be salts of a postulated ruthenic acid and are more soluble in water and more stable than the perruthenates. The ruthenates, as well as the perruthenates, are colored; their extinction coefficients are known. Several analytical uses of the highly colored compounds are described.<sup>(28,32,48)</sup> The absorption spectra of the perruthenate and ruthenate ions are given in Fig. 3.2.<sup>(48)</sup> Perruthenates are analogous to permanganates and to perrhenates; however, potassium perruthenate is not isomorphous with potassium permanganate. Likewise, ruthenates are analogous to manganates and rhenates.

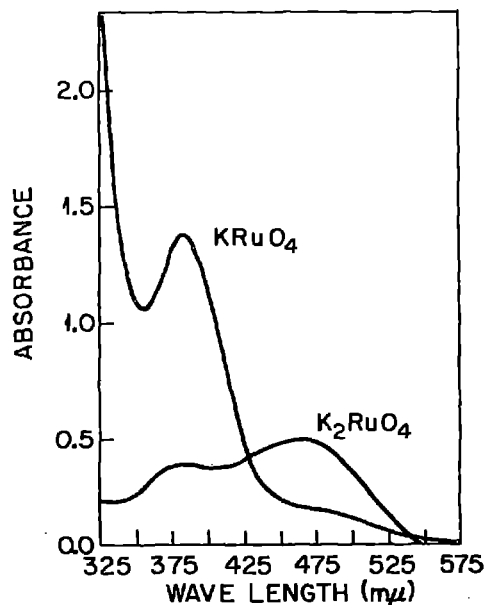


Fig. 3.2. Spectrophotometric Curves for  $K_2RuO_4$  and  $KRuO_4$ ;  $[Ru] = 0.1$  mg/ml. [Reprinted from Anal. Chem. 27, 1186 (1955).]

3.2.3 Halogen Compounds and Amines. Specific halogen compounds and complexes of di-, tri-, and tetravalent ruthenium are known. The chlorination of ruthenium metal produces ruthenium trichloride and possibly ruthenium tetrachloride, but ruthenium pentachloride has not been isolated. Commercial ruthenium chloride is usually a mixture of the trichloride and tetrachloride.<sup>(19)</sup> Ruthenium dichloride is formed by the reduction of the chlorides of higher-valent ruthenium and is deep blue. The chloro compounds of ruthenium are usually colored; in this respect they differ from the chloro compounds of osmium. Many soluble chloro complexes of ruthenium have been studied,<sup>(51)</sup> and slightly soluble chlororuthenates and chloroperruthenates have been prepared.<sup>(29)</sup> Double salts of the alkali-metal and of alkaline-earth elements with the chloro compounds of ruthenium have been prepared, most of which are slightly soluble in water. All the chloro forms of ruthenium encountered in radiochemistry are easily reduced to ruthenium metal in acid solution by use of zinc or

magnesium metal. Most tracer forms of ruthenium in a chloride system behave in a predictable manner.

Although a large number of complexes of ruthenium(II) exist, only a few have been isolated; among them are the amines,  $[\text{Ru}(\text{dipy})_3]\text{X}_2$ ,<sup>(46)</sup> and the nitrosyls,  $\text{RuNOX}_3$ , where X is Cl, Br, or I. Some characteristics of some of the amines of ruthenium(II) are as follows:<sup>(46,\*)</sup>

A. Hexamines: all red.

B. Pentamines.

$[\text{Ru}(\text{NH}_3)_5\text{SO}_3]$ , 2  $\text{H}_2\text{O}$ : colourless.

$[\text{Ru}(\text{NH}_3)_5\text{SO}_2]\text{Cl}_2$ ,  $\text{Br}_2$ ,  $(\text{NO}_3)_2$ ,  $\text{S}_2\text{O}_8$ ,  $\text{SO}_4$ , 2  $\text{H}_2\text{O}$ : all red.

C. Tetramines.

$[\text{Ru}(\text{NH}_3)_4\text{SO}_3\text{H}]_2$ : colourless insoluble.

$[\text{Ru}(\text{NH}_3)_4\text{SO}_2\text{Cl}]\text{Cl}$ , red:  $[\text{SO}_4\text{H}]$  red:  $-\text{Br}]\text{Br}$ , brown, very slightly soluble:  $-(\text{OH}_2)](\text{NO}_3)_2$ , yellow:  $-(\text{OH}_2)]\text{S}_2\text{O}_8$ , pale yellow.

D. Diammines.

$\text{Na}_4[\text{Ru}(\text{NH}_3)_2(\text{SO}_3)_2(\text{SO}_3\text{H})_2]$ , 6  $\text{H}_2\text{O}$ , colourless, slightly soluble.

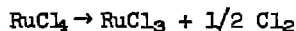
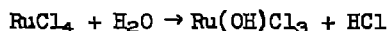
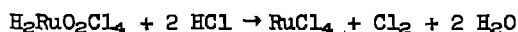
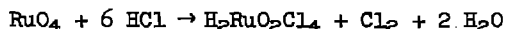
Ammonium salt, 4  $\text{H}_2\text{O}$ , colourless, readily soluble.

Ruthenium(III) is a common valence form of rutheruthenium. The fluoride of ruthenium(III) is sparingly soluble in water and in dilute solutions of acids and alkalis. The pentafluoride has also been reported.<sup>(12)</sup> The better-known coordination complexes of ruthenium(III) are the halogen complexes and the haloamines. The only known halo complexes of ruthenium(III) are the chloro and bromo forms. General forms include  $\text{MRuX}_4$  to  $\text{M}_4\text{RuX}_7$  and  $\text{M}_2[\text{Ru}(\text{NO})\text{X}_5]$ . The tetrahalo salts include water in the molecule, that is,  $\text{M}[\text{RuX}_4(\text{H}_2\text{O})_2]$ , the removal of which destroys the complex. However, the pentachloro complex,  $\text{K}_2[\text{RuCl}_5(\text{OH}_2)]$ , can be dehydrated at  $200^\circ\text{C}$  to yield  $\text{K}_2[\text{RuCl}_5]$ .<sup>(46)</sup> Common haloamines include  $[\text{Ru}(\text{NH}_3)_5\text{X}]^{2+}$ ,  $[\text{Ru}(\text{NH}_3)_4\text{X}_2]^+$ , and  $[\text{Ru}(\text{NH}_3)_3\text{X}_3]^0$ , where X is Cl or Br.

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Information taken from N. V. Sidgwick, The Chemical Elements and Their Compounds, Vol. II, p. 1465, Oxford, London, 1950, with permission of the publisher.

The halo complexes of ruthenium(IV) are of the type  $M_2[RuX_6]$  and  $M_2[RuX_5OH]$ , where X is Cl or Br. Anhydrous  $RuCl_4$  is unknown, but the hydrated tetrachloride has been isolated as  $RuCl_4 \cdot 5H_2O$ . Other chloro compounds of ruthenium include  $Ru(OH)Cl_3$  and  $Ru(NO)Cl_3$ . Possible reactions involving chlororuthenium species are: (46,\*)



The approximate potentials of the more important couples of ruthenium are as follows: (29)\*\*

	Volts 25°
$Ru = Ru^{++} + 2 e^-$ - - - - -	-0.45
$Ru^{++} + 5 Cl^- = RuCl_5^{--} + e^-$ - - - - -	-0.3
$RuCl_5^{--} + H_2O = RuCl_5OH^{--} + H^+ + e^-$ - - - - -	-1.3
$RuCl_5OH^{--} + 3 H_2O = RuO_4 + 5 Cl^- + 7 H^+ + 4 e^-$ - - - - -	-1.5
$Ru + 6 OH^- = RuO_3^{--} + 3 H_2O + 4 e^-$ - - - - -	-0.3
$RuO_3^{--} + 2 OH^- = RuO_4 + H_2O + 2 e^-$ - - - - -	-0.6

3.2.4 Nitrosyl Complexes. A complete description of the nitro nitrosylruthenium system of ionic species and their behavior would be very lengthy. The work in this field has been followed seriously by many (15,34,54) because of the direct problems that have arisen with ruthenium in processes involving nitrate systems. Isolation of some of these complexes and, in some cases, nondestructive measurements have

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\* Information taken from N. V. Sidgwick, The Chemical Elements and Their Compounds, Vol. II, pp. 1476, Oxford, London, 1950, with permission of the publisher.

\*\* Information taken from W. M. Latimer and J. H. Hildebrand, Reference Book of Inorganic Chemistry, rev. ed., pp. 417, Macmillan, New York, 1947, with permission of the publisher.

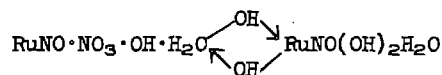
provided some knowledge about the many forms in which ruthenium may exist in nitrate systems. Numerous studies have been made of the various oxidation states of ruthenium in nitrate and other systems.<sup>(6,18,40)</sup> Some ruthenium nitrosyls are extractable, which property aids in the identification of the species, whereas others are not extractable, not easily precipitated, and not directly reduced.

Only with a knowledge of what species of ruthenium may possibly be encountered can carrier or carrier-free methods of assay be used in a nitrate system with confidence. In process waste streams from nitrate systems, the radoruthenium does not always accompany ruthenium carrier unless the active and inactive ruthenium are oxidized and/or reduced vigorously.

Nitro and nitrate complexes of nitrosylruthenium are formed from  $\text{RuO}_4$  and ruthenium alloys by the action of nitric acid or the oxides of nitrogen.<sup>(15)</sup> These forms of ruthenium often occur in processes, especially those in which solvent-extraction systems are used; they must be removed by deposition<sup>(21,27)</sup> or be chemically changed to an unextractable form.<sup>(13)</sup>

The isolation and identification of some of the nitratooquo nitrosylruthenium complexes having the general formula  $\text{RuNO}(\text{NO}_3)_x(\text{OH})_{3-x}(\text{H}_2\text{O})_2$  have been reported.<sup>(15)</sup> Some of the properties of these compounds are listed in Table 3.4.<sup>(15)</sup> The methods of formation of some of these complexes and others encountered in radiochemistry are suggested in Fig. 3.3.<sup>(25)</sup> Many of the nitrate complexes of ruthenium are derived from the parent compound ruthenium nitrosyl hydroxide,  $\text{RuNO}(\text{OH})_3$ .

By the hydrolysis of the nitrate complexes, polynuclear species such as the following are formed.<sup>(14)</sup>



The polyhydroxy complexation of radoruthenium in alkaline solution occurs frequently but is not fully understood. The formation of six- to eight-ruthenium-atom polymers, which can be precipitated as hydrated

Table 3.4. Nitrosylruthenium Complexes<sup>(\*)</sup>

Name	Complex Formula	Description
Nitrosylruthenium hydroxide	$\text{RuNO}(\text{OH})_3$	Dark brown solid. Readily peptised by water, acids, and alkalis when freshly precipitated.
Nitrosylruthenium hydro-sulphide	$\text{RuNO}(\text{SH})_{2.5}(\text{OH})_{0.5}(\text{H}_2\text{O})_{0.67}$	Dark brown solid. Insoluble in water and in dilute acids and alkalis.
Trinitrato Nitrosylruthenium	$[\text{RuNO}(\text{NO}_3)_3(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$	Rose-red deliquescent solid. Soluble in water, ethers, ketones, alcohols, esters, etc.
Dinitrato nitrosylruthenium	$[\text{RuNO}(\text{NO}_3)_2\text{OH}(\text{H}_2\text{O})_2]$	Reddish brown deliquescent solid. Soluble in water, ethers, ketones, etc.
Mononitrato nitrosylruthenium	$[\text{RuNO} \cdot \text{NO}_3 \cdot (\text{OH})_2(\text{H}_2\text{O})_2]$	Brown hygroscopic solid. Soluble in water and lower ketones but not in ethers.
	$(\text{RuNO})_2\text{NO}_3(\text{OH})_5$	Brown solid. Soluble in water but not in ethers and lower ketones.
Polynuclear aquo-nitrato complexes		Brown solids. Solubility in water and in ketones dependent on composition and method of preparation.
Sodium Tetranitronitrosyl-ruthenium	$\text{Na}_2[\text{RuNO}(\text{NO}_2)_4\text{OH}]2\text{H}_2\text{O}$	Orange crystalline salt. Soluble in water, ketones, alcohols, etc.
	$\text{Ru}_2\text{N}_8\text{O}_{15}$	Orange-brown deliquescent solid. Formed only under anhydrous conditions. Soluble in ketones, ethers, alcohols, etc.
Oxalatonitratonitrosyl-ruthenium	$\text{RuNO} \cdot \text{NO}_3 \cdot \text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	Pink crystalline solid. Soluble in water, insoluble in organic solvents.
Sulphatonitratonitrosyl-ruthenium	$[\text{RuNO} \cdot \text{NO}_3 \cdot \text{SO}_4(\text{H}_2\text{O})_3]$	Orange hygroscopic solid. Soluble in water.
Hydrogen tetrachlorohydroxo-nitrosylruthenate	$\text{H}_2[\text{RuNOCl}_4\text{OH}]2\text{H}_2\text{O}$	Purple deliquescent solid. Soluble in water and alcohols.
Nitrosylruthenium fluoride	$\text{RuNO} \cdot \text{F}_{2.6}(\text{OH})_{0.4}$	Dark brown powder. Contains no complexed fluoride.

\* Information taken from Table 1 of J. M. Fletcher et al., J. Inorg. & Nuclear Chem. 1, 379 (1955) with permission of Pergamon Press, Inc.

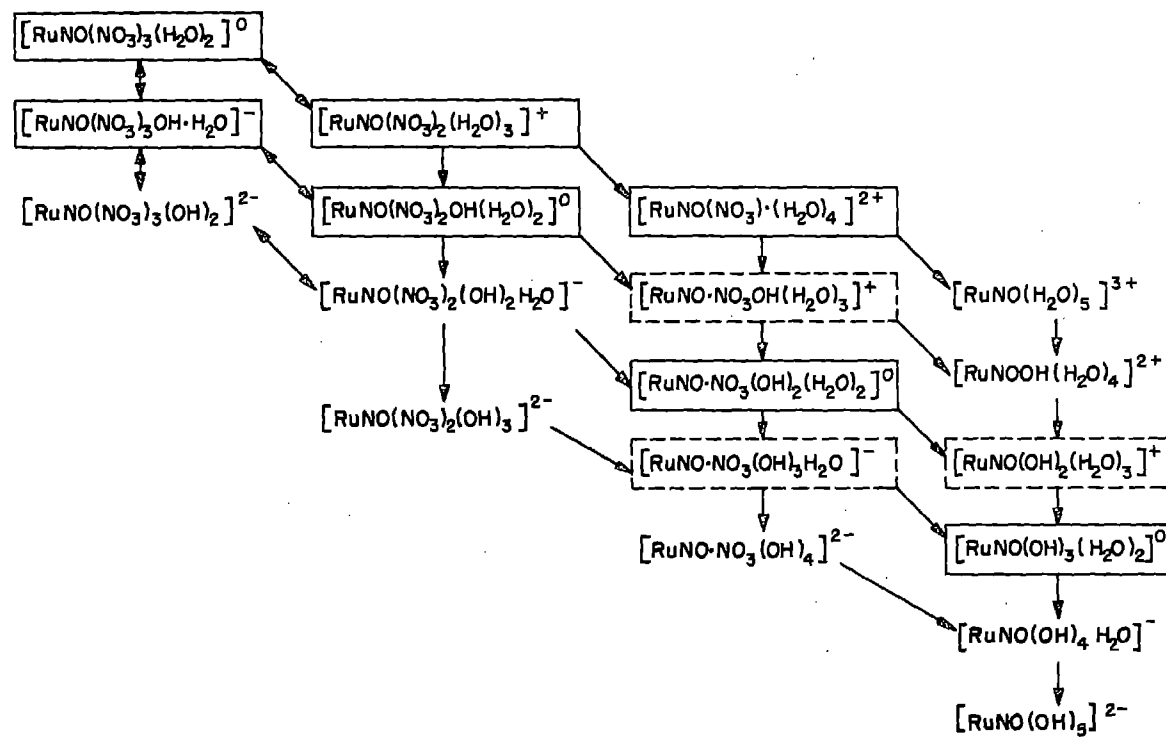


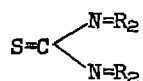
Fig. 3.3. Methods of Formation of Nitrate-nitrosyl Complexes of Ruthenium in Aqueous Solution.  
 [Taken from Trudy Komissii Anal. Khim., Akad. Nauk S.S.S.R., Inst. Geokhim. i Anal. Khim. 2, 148 (1958).]

oxides or remain stable in solution, has been reported.<sup>(44)</sup> Radio-ruth in this state has been recognized as extremely stable, defying oxidation and reduction.<sup>(39)</sup> Interchange of ruthenium carrier and rutheruthenium, when present in these stable polymers, requires many hours of digestion at 60 to 80°C. Such compounds as sodium gluconate and sugars complex ruthenium strongly in alkaline solutions.<sup>(44)</sup> The unpredictable behavior of rutheruthenium has been observed in radioactive waste-disposal systems in which alkaline solutions are used.

3.2.5 Cyano and Thio Complexes. Ruthenium(II) forms complexes, all of which are of the type  $M_4[Ru(CN)_6]$  corresponding to the ferrocyanides.<sup>(46)</sup> When chlorine is passed into a solution of potassium rutheruthenocyanide,  $K_4[Ru(CN)_6]$ , stable  $Ru(CN)_3 \cdot 5H_2O$  can then be isolated after precipitation with  $H_2SO_4$ .<sup>(46)</sup>

The thio complexes of ruthenium are usually highly colored and are used mostly in ionic assays.<sup>(11,26,52,53)</sup> These complexes and others<sup>(1)</sup> have not been used directly in radiochemistry, although their applications in ion-exchange studies<sup>(37)</sup> have been reported. However, direct sulfide precipitations of ruthenium have been used in radio-ruthenium separations.<sup>(16)</sup>

The thio complexes of ruthenium have received considerable attention in spectrophotometric work. Strongly colored thioruthenium complexes are formed with thiourea and derivatives of thiourea of the general form<sup>(43)</sup>



where R is H or the alkyl, aryl, or  $NER_1$  group. These complexes are formed in a strongly acid solution, preferably hydrochloric acid.

Ruthenium(III) and ruthenium(IV) in perchloric acid solution form blue-green chelate complexes with thiourea of the types  $Ru(III)[HNC-SNH_2]^{++}$  and  $Ru(III)[HNC-SNH_2]_3$ , respectively.<sup>(43)</sup> Ruthenium(III) and ruthenium(IV) in perchloric acid react similarly with thiocyanate to form  $Ru(CNS)^{++}$ . Ruthenium(IV) is reduced at the expense of the thiocyanate.<sup>(52)</sup> The

compounds related to thiourea have been investigated for formation of complexes with ruthenium.<sup>(26)</sup> A summary of the thiourea-type reagents for ruthenium is presented in Table 3.5.<sup>(43)</sup>

Table 3.5. Colorimetric Thiourea-type Reagents for Ruthenium<sup>a(\*)</sup>

<u>No.</u>	<u>Reagent</u>	<u>Color of Product</u>	<u>Limit of Detection, Ru <math>\gamma</math>/ml</u>
1	$\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{S}=\text{C} \\ \diagdown \\ \text{NHCH}_3 \end{array}$	Blue	0.08
2	$\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{S}=\text{C} \\ \diagdown \\ \text{NHC}_2\text{H}_5 \end{array}$	Blue	0.08
3	$\begin{array}{c} \text{N}(\text{CH}_3)_2 \\ \diagup \\ \text{S}=\text{C} \\ \diagdown \\ \text{NHCH}_3 \end{array}$	Red	0.13
4	$\begin{array}{c} \text{N}(\text{CH}_3)_2 \\ \diagup \\ \text{S}=\text{C} \\ \diagdown \\ \text{N}(\text{CH}_3)_2 \end{array}$	Violet	0.13
5	$\begin{array}{c} \text{NHNH}_2 \\ \diagup \\ \text{S}=\text{C} \\ \diagdown \\ \text{NH}_2 \end{array}$	Red $\rightarrow$ green	0.14
6	$\begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{S}=\text{C} \\ \diagdown \\ \text{NHNHC}_6\text{H}_5 \end{array}$	Violet	----
7	$\begin{array}{c} \text{NHNHC}_6\text{H}_5 \\ \diagup \\ \text{S}=\text{C} \\ \diagdown \\ \text{NHC}_6\text{H}_5 \end{array}$	Violet	0.025
8	$\begin{array}{c} \text{NHC}_6\text{H}_5 \\ \diagup \\ \text{S}=\text{C} \\ \diagdown \\ \text{N}-\text{C}_6\text{H}_5 \\   \\ \text{NH}_2 \end{array}$	Violet	0.017
9	$\begin{array}{c} \text{NHC}_6\text{H}_5 \\ \diagup \\ \text{HS}-\text{O} \\ \diagdown \\ \text{N}-\text{NHC}_6\text{H}_5 \end{array}$	Violet	0.025
10	$\begin{array}{c} \text{NHNH}_2 \\ \diagup \\ \text{S}=\text{C} \\ \diagdown \\ \text{NHNH}_2 \end{array}$	Red	0.6
11	$\begin{array}{c} \text{NH}-\text{NHC}_6\text{H}_5 \\ \diagup \\ \text{S}=\text{C} \\ \diagdown \\ \text{NH}-\text{NHC}_6\text{H}_5 \end{array}$	Violet	----

<sup>a</sup> The ruthenium compounds of 5, 7, and 8 (and perhaps others) can be extracted with ether. Osmium reacts with 6, 7, 9, 11 (green colors) but not with 2, 3, 5.

\* Taken from Table 100 of E. B. Sandell, Colorimetric Determination of Traces of Metals, 3 ed., p. 782, Interscience, New York, 1959, with permission of the publisher.

#### 4. Analysis of Materials that Contain Radioactive Ruthenium

##### 4.1 Types and Pretreatment of Samples

The following is a list of the types of samples that may contain radioruthenium; radiochemical procedures suggested for use in their analysis are indicated (the procedures are appended):

4.1.1 Fuel Process Solutions, etc. These samples contain various amounts of fission products in aqueous solutions.

Suggested Procedures: Nos. 1, 2, 3, 8, 10, 12, 13, 14, and gamma-ray spectrometry if possible.

4.1.2 Organic Solvents. Suggested Procedures: Nos. 4, 10, 12, and gamma-ray spectrometry.

4.1.3 Large Volumes of Water. If low concentrations of activity necessitate the handling of large volumes of water, special techniques are sometimes in order.

Suggested Procedures: Nos. 3, 5, 6, and possibly gamma-ray spectrometry.

4.1.4 Soil Samples. Samples of earth and mud should be dried and weighed prior to any other treatment since it is usual to report the results in terms of the weight of soil.

Suggested Procedures: Nos. 1, 2, 7, 8, 9, 11, 19, and possibly gamma-ray spectrometry.

4.1.5 Vegetation and Biological Material. Vegetation should be dried, powdered, ashed if the sample is very bulky, and weighed. Procedure 2 may be used without further pretreatment of the sample. Procedure 3 requires a pretreatment by boiling with sulfuric acid. If there is sufficient radioactivity, it may be possible to use gamma-ray spectrometry without destruction of the powdered material.

Wet-ashing is required for most biological materials; any of the following procedures can then be used: No. 2, 7, 8, 20, or gamma-ray spectrometry.

4.1.6 Solid Uranium Salts and Ruthenium-Uranium Alloys. Care must be exercised in the dissolution of various solids to prevent oxidation of ruthenium to the tetroxide and the resultant loss by volatilization. Uranium trioxide and  $\text{UO}_2\text{F}_2$  will dissolve in hydrochloric acid solution. Other solids of these types may dissolve in sulfuric acid if a little hydrochloric acid is added to prevent oxidation. Fusion with sodium hydroxide and potassium nitrate or with potassium carbonate and sodium peroxide has been used to dissolve  $\text{UF}_4$ . After the sample is dissolved, Procedure 1, 2, 3, 12, or gamma-ray spectrometry can be used.

#### 4.2 Isolation of Ruthenium

4.2.1 Electrodeposition. The polarographic separation of  $\text{Ru}^{103,106}$  from fission product solution has been reported.<sup>(31)</sup> The ruthenium, together with technetium, amalgamates with the dropping mercury at -1.55 volts vs. the S.C.E. The mercury is removed from the fission-product solution by falling through it into carbon tetrachloride (see Procedure 13).

In the electroplating of ruthenium, the compound ruthenium nitroschloride,  $\text{RuNOCl}_3$ , is generally used. A suggested plating mixture and conditions are:<sup>(\*)</sup>

8 g of Ru as  $\text{RuNOCl}_3$   
80 ml of sulfuric acid  
1 gal of  $\text{H}_2\text{O}$   
Current density, 20 to 30 amp/ft<sup>2</sup>  
Temp., 130 to 170°F

During the preparation of ruthenium sources at the Oak Ridge National Laboratory, the synthesis of  $\text{RuNOCl}_3$  twice resulted in unexplained explosions.<sup>(41)</sup>

An electrolytic method for determining radioruthenium is described in Procedure 14.<sup>(7)</sup>

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\* Information taken from Metal Finishing Guidebook, 28th ed., p. 386, Metals and Plastics Publication, Inc., Westwood, N. J., 1960, with permission of the publisher.

4.2.2 Ion-exchange Separations. In the most promising ion-exchange separations of ruthenium, anion-type resins are used. Several types of resins have been studied carefully.<sup>(37)</sup> The adsorption of ruthenium from solutions of various acids onto Dowex-2 resin has been studied.<sup>(5)</sup> The adsorption characteristics are indicated in Fig. 4.1. These studies

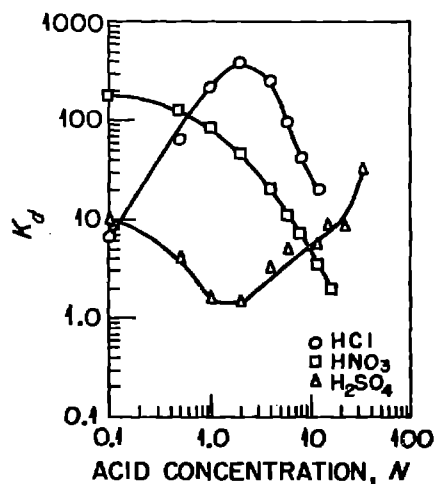


Fig. 4.1. Equilibrium Adsorption of Ru(IV) onto Dowex-2 from Mineral Acids. [Data taken from Anal. Chem. 31, 324 (1959), Figs. 1, 2, and 3.]

are interesting; however, ion-exchange has not been used extensively in radioruthenium separations. The use of cation-type exchangers for the separation of radioruthenium has not shown promise, perhaps because of the ease of formation of anionic type complexes. The unpredictable behavior of ruthenium toward cation exchangers, particularly in process type samples, has been observed.<sup>(50)</sup> For an appreciation of the ion-exchange behavior of ruthenium in nitrate systems, the original literature<sup>(2,4,5)</sup> should be read.

The ion-exchange properties of ruthenium have received considerable study relative to fission-product waste-disposal schemes. A summary of the results of a rather comprehensive investigation of the

exchange characteristics of various minerals with respect to ruthenium under usual waste-disposal conditions is given in Table. 4.1. (39)

Table 4.1. Minerals Exhibiting the Highest Percentage of Removal of Ruthenium in Order of Their Relative Effectiveness(\*)

<u>Mineral</u>	<u>Amount Removed after Indicated Contact Time, %</u>		
	<u>One day</u>	<u>Four days</u>	<u>Four days plus 16 hr at 60°C</u>
<u>Reducing Conditions, pH 7</u>			
Copper in conglomerate	53.7	73.7	92.7
Descloizite	46.3	72.3	91.5
Copper	45.9	72.8	91.1
Fuchsite	72.2	80.7	89.7
Zirconium phosphate	57.0	79.0	87.0
Cuprite	56.2	78.6	85.7
Chalcocite	29.3	48.3	82.2
Barium chromate	49.7	78.6	81.0
Smaltite	31.3	62.4	77.8
Glaucinite	30.1	61.1	76.6
<u>Oxidizing Conditions, pH &gt; 13</u>			
Rammelsbergite		44.4	
Chalcocite		26.1	
Diginite in pyrite		25.2	
Copper in conglomerate		25.2	
Fuchsite		24.7	
Limonite		21.5	
Realgar		21.1	
Copper (native)		19.2	
Psilomelane		18.8	
Sphalerite		17.4	

\* Taken from S. J. Rimshaw and D. C. Winkley, ORNL CF-60-4-17 (April, 1960), with permission of the authors.

4.2.3 Distillation. The distillation of ruthenium as ruthenium tetroxide, usually from an acid solution that contains a strong oxidant,

is accomplished with ease (see Sec. 3.2.1). It affords a separation scheme for ruthenium from other fission products that is rapid and complete and for which there is excellent likelihood of interchange between carrier and radioactive ruthenium.

Since many of the procedures include a distillation step, a typical still for the distillation of ruthenium as ruthenium tetroxide,  $\text{RuO}_4$ , is shown in Fig. 4.2.

4.2.4 Other Techniques. The direct reduction of ruthenium to the metal with magnesium metal suffices to a limited extent to separate ruthenium from other fission products.

In another direct technique, ruthenium carrier and radoruthenium are extracted as a nitrosyl compound into tributyl phosphate—Amsco solution.<sup>(45)</sup> Still another direct technique exploits the high extractability of ruthenium tetroxide into carbon tetrachloride from acid solutions (see Sec. 3.2.1).<sup>(33)</sup>

#### 4.3 Determination of Radioactive Ruthenium

The choice of counting instrumentation for radoruthenium is determined by the ratio of  $\text{Ru}^{103}$  to  $\text{Ru}^{106}$  and/or the nuclide sought.

4.3.1 Beta Counting. The end-window Geiger-Mueller counter is used when  $\text{Ru}^{106}$  is the major ruthenium activity present;  $\text{Ru}^{106}$  is usually determined by counting the more energetic beta particles from the  $\text{Rh}^{106}$  daughter. The determination is commonly made by inserting an aluminum absorber between the sample mount and tube window to absorb the beta activities of  $\text{Ru}^{106}$  and  $\text{Ru}^{103}$  (see Figs. 4.3 and 4.4).<sup>(21)</sup> The absorber should allow most of the beta particles from  $\text{Rh}^{106}$  to penetrate; a suitable correction is made for loss of  $\text{Rh}^{106}$  beta in the absorber.

4.3.2 Gamma Counting. Gamma-ray spectrometry has been very useful in the determination of various radionuclides found in mixed fission products. It is frequently possible to determine ruthenium by means of gamma-ray spectrometry without any chemical separation. Spectrometric

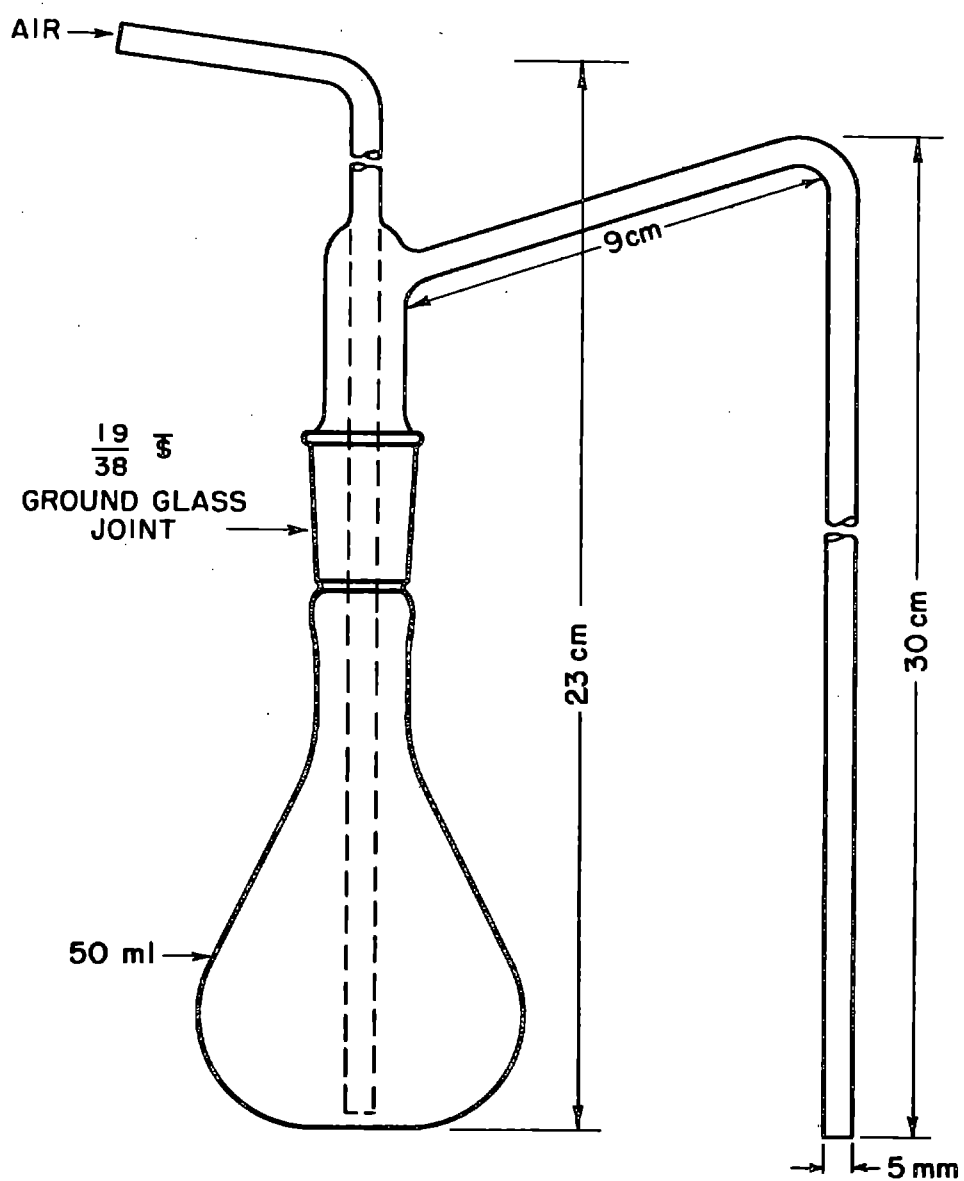


Fig. 4.2. Flask for the Distillation of Ruthenium as  $\text{RuO}_4$ .

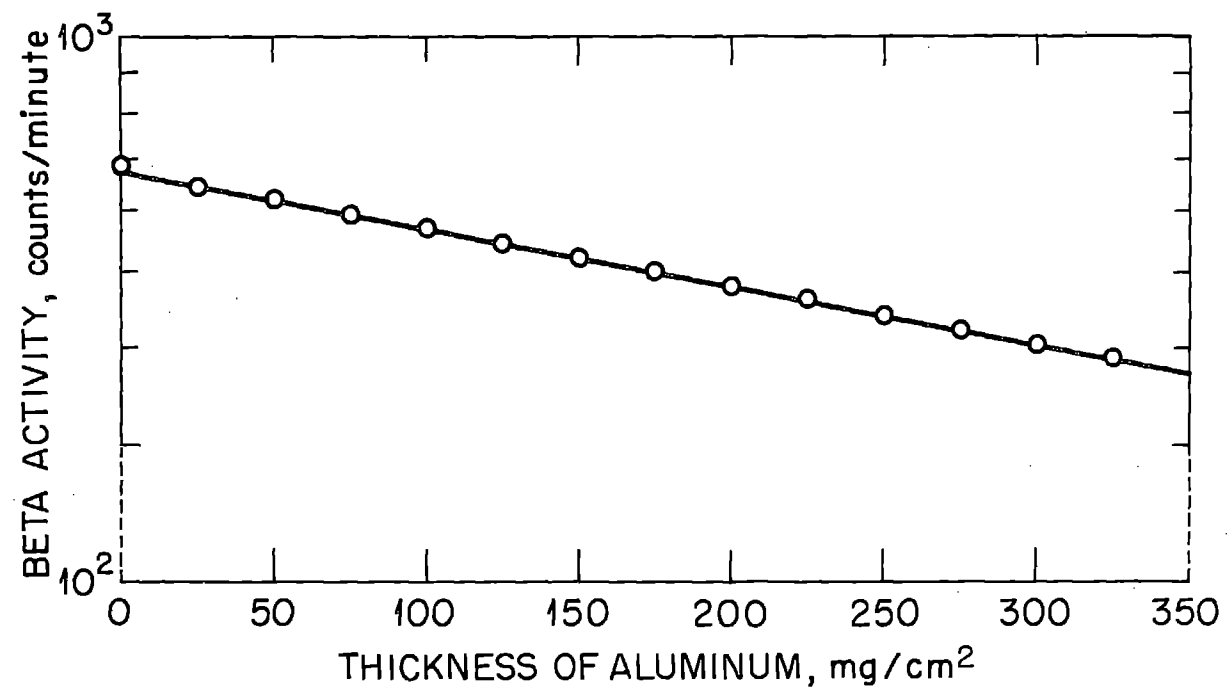


Fig. 4.3. Results of a Beta Absorption Study of  $\text{Ru}^{106}\text{-Rh}^{106}$ .

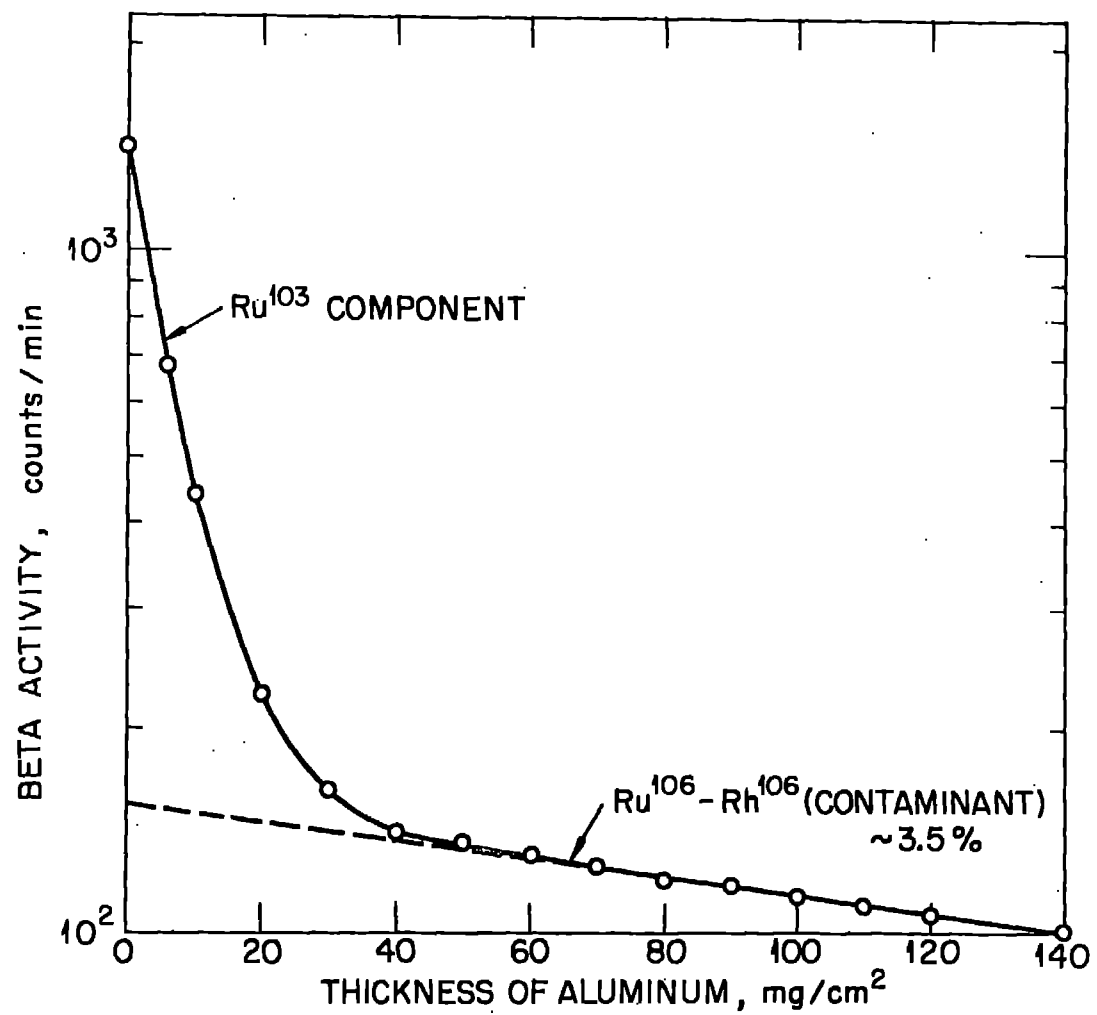


Fig. 4.4. Results of a Beta Absorption Study of  $\text{Ru}^{103}$ .

techniques vary with sample type, sample history, activity level, and the type of spectrometer available. It is usually desirable to avoid chemical separations if a gamma-ray spectrometer will do the job. References 8, 10, 22, 30, 35, and 42 give the information and describe the techniques needed. A gamma-ray spectrometer is frequently used to determine  $\text{Ru}^{103}$  in the presence of  $\text{Ru}^{106}$ . (8,10,22,30,35,38,42) Beaufait and Lukens<sup>(3)</sup> have compiled considerable data on counting procedures. The gamma spectra of  $\text{Ru}^{106}$ - $\text{Rh}^{106}$  and of  $\text{Ru}^{103}$  are shown in Figs. 4.5 and 4.6, respectively,

4.3.3 Selected Procedures. Selected radiochemical procedures for the determination of ruthenium are appended. Some of these have been copied verbatim from the source indicated. When a procedure refers to references given in the source, those references have also been copied and are listed at the end of the procedure.

The authors have had experience with Procedures 1, 3, 6, 7, 9, 10, and 19. Of these, Procedures 1, 3, and 10 have been used extensively for samples of mixed fission products from process streams, etc. Procedures 1 and 10 include distillations from perchloric acid, whereas Procedure 3 does not require a distillation. Procedure 10 is used for samples of organic solvents. Procedure 6 is an adaptation of Procedure 3 and is used to separate ruthenium from large volumes of water. Procedure 7 is a distillation from potassium permanganate solution; it works well with vegetation or biological material. Procedure 9 has been used extensively with samples of soil. The leach solution of 3 M HCl—0.1 M HF mentioned in Procedure 8 has been tried with success on insoluble materials. Procedure 19 has also been used for environmental samples after they were leached with 3 M HCl—0.1 M HF. No one of the procedures listed above has proved satisfactory for all types of samples.

Many of the analyses of process streams (when the history and age of the material is known) have been done by means of gamma spectrometry without destruction of the sample. It is highly recommended that this method be used whenever possible.

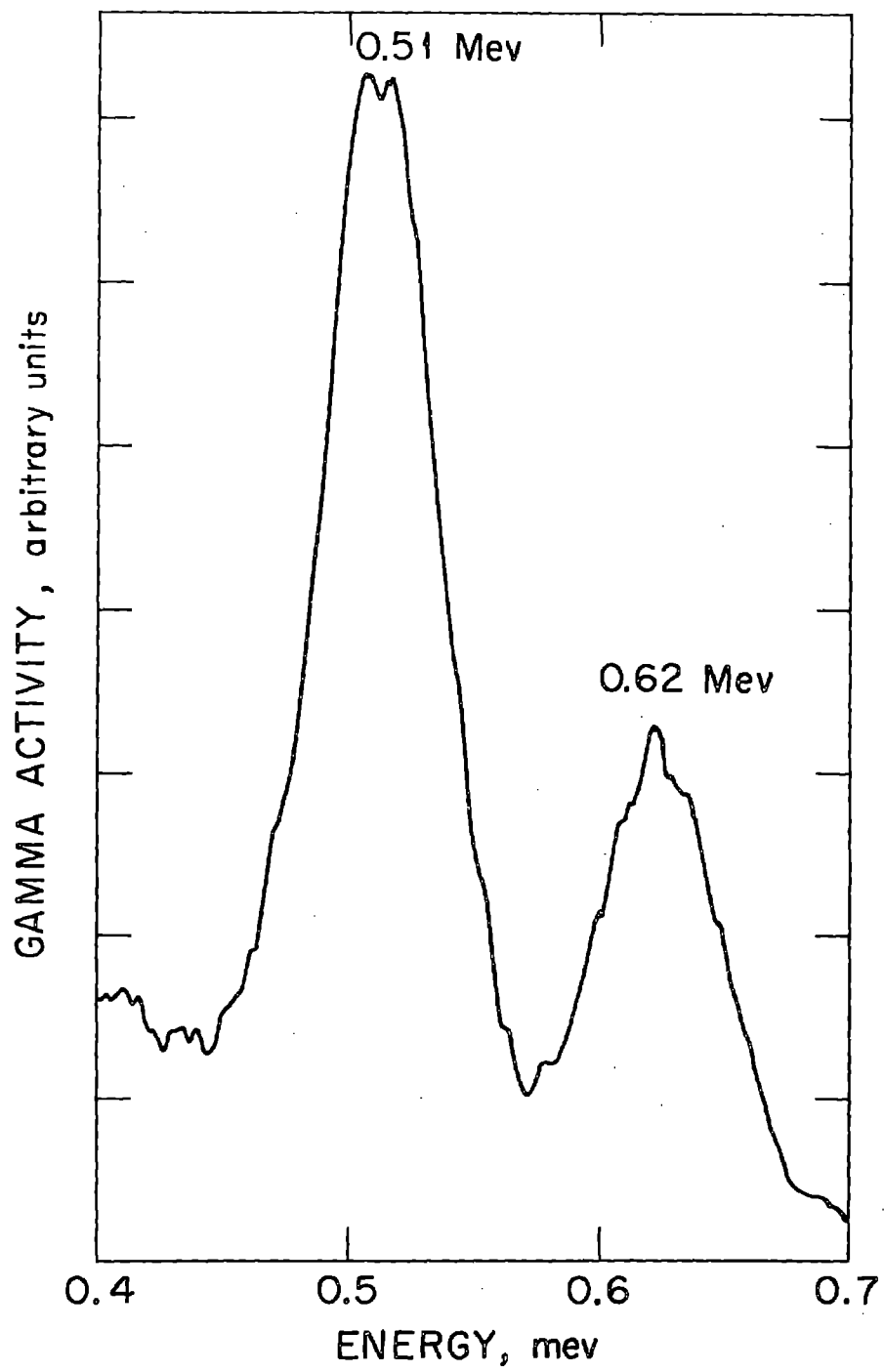


Fig. 4.5 Gamma Spectrum of Ru<sup>106</sup>-Rh<sup>106</sup> (2 x 2 in. NaI crystal).

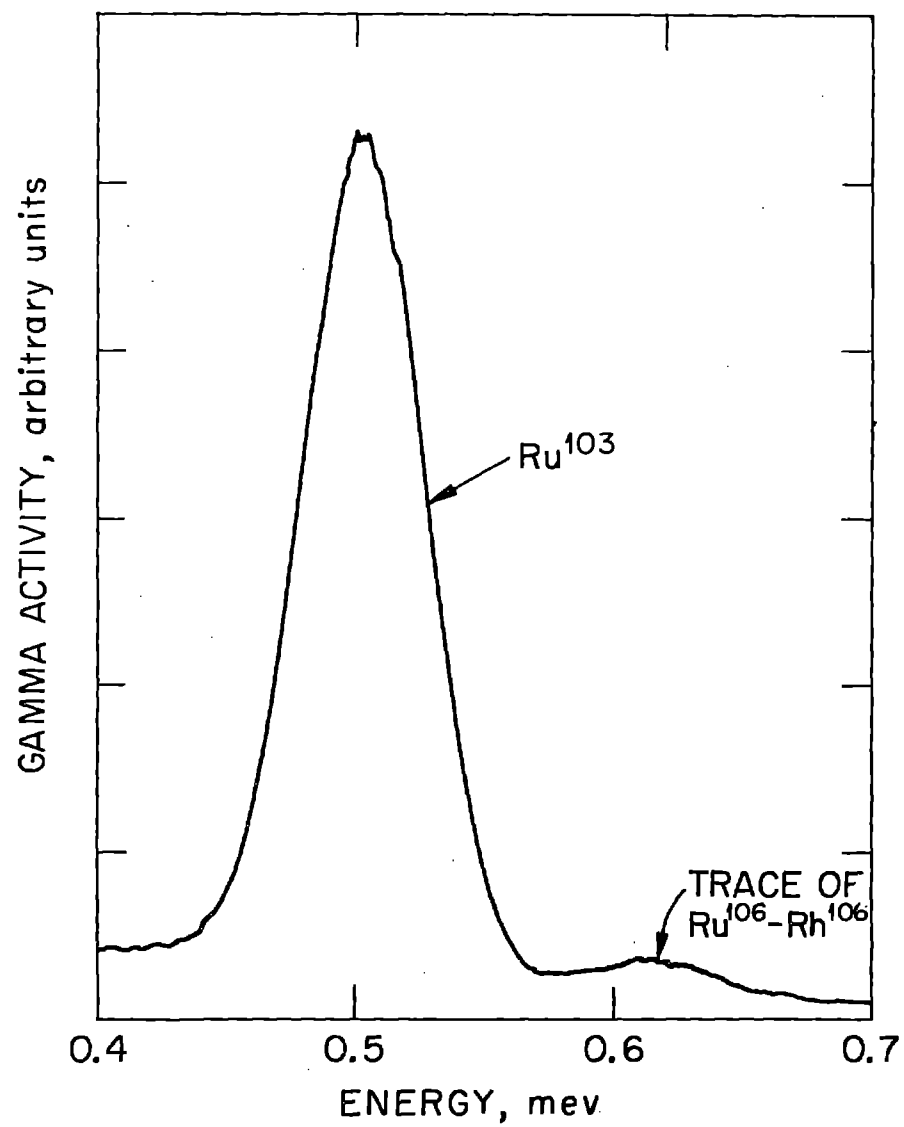


Fig. 4.6 Gamma Spectrum of  $\text{Ru}^{103}$  (2 x 2 in. NaI crystal).

## PROCEDURE 1

### Improved Determination of Ruthenium Activity in Fission

Source: Glendenin, L. E., Paper No. 260, p. 1549, in Coryell, C. D. and Sugarman, N., Radiochemical Studies: The Fission Products, Book 3, McGraw-Hill, New York, 1951

#### A. Preparation and Standardization of Carrier

Commercial ruthenium chloride is usually a mixture of the hydrated tri-chloride and tetrachloride. Dissolve 26 g of commercial ruthenium chloride in 1 liter of 0.1M HCl. Pipet 5 ml of carrier solution into a 250-ml Erlenmeyer flask and add 25 ml of H<sub>2</sub>O and 2 ml of 12M HCl. Add 0.4 g of powdered magnesium metal in small portions, shaking after each addition. Add a few drops of Aerosol solution to minimize frothing, and boil gently until the ruthenium precipitate is well coagulated and the supernatant solution is clear and colorless. Continue boiling for 2 min. Add 10 ml of 12M HCl slowly to remove the excess magnesium and boil again for 2 min. If the supernatant solution is not perfectly clear and colorless at this point, add another small portion of magnesium and boil (if the reduction is still incomplete, discard the sample and start another). Filter quantitatively with suction onto a weighed sintered-glass crucible. Wash three times with 5 ml of hot H<sub>2</sub>O, three times with 5 ml of 95 per cent ethanol, and three times with ether, rinsing down the inside of the crucible with each portion of the wash liquid. Wipe the outside of the crucible carefully with Kleenex or lintless cloth, and dry at 110°C for 10 min. Cool in a desiccator and weigh.

#### B. Procedure

Step 1. Place not more than 5 ml of a uranyl nitrate sample in a distillation flask (Note 1) and add 2 ml of ruthenium carrier, 10 mg each of I<sup>-</sup> and Br<sup>-</sup> carriers, 1 g of NaBiO<sub>3</sub>, 1 ml of 85 per cent H<sub>3</sub>PO<sub>4</sub>, and 10 ml of 70 per cent HClO<sub>4</sub>. Heat gently to boiling and then distill the ruthenium rapidly (avoid bumping) into 12 ml of 6M NaOH (Note 2) in a 50-ml centrifuge tube placed in an ice bath (Notes 3 and 4).

PROCEDURE 1 (Continued)

Step 2. Add 3 ml of ethanol to the distillate, heat just to boiling by swirling over a free flame, and centrifuge (Note 5). Suspend the precipitate in 10 ml of  $H_2O$  containing 1 ml of 6M NaOH (Note 2), heat just to boiling, and centrifuge.

Step 3. Dissolve the precipitate by heating just to boiling in 2 ml of 6M HCl, and add 10 ml of  $H_2O$ . Add 0.2 g of powdered magnesium metal in small portions, shaking after each addition. Add a few drops of Aerosol solution to minimize frothing, and boil gently until the ruthenium precipitate is well coagulated. Continue boiling for 2 min. Add 5 ml of 12M HCl slowly to remove the excess magnesium, and boil again for 2 min.

Step 4. Filter with suction onto a weighed filter-paper disk in a small Hirsch funnel (Note 6). Wash three times with 5 ml of hot  $H_2O$ , three times with 5 ml of 95 per cent ethanol, and three times with 5 ml of ether. Dry the precipitate at  $110^{\circ}C$  for 10 min, weigh, and mount (Note 7).

Notes. 1. An all-glass still of 50 ml capacity with an arrangement for slowly passing air through the distillant (one to two bubbles per second) is necessary throughout the distillation to prevent suckbacks.

2. The 6M NaOH reagent should be kept free of silica by storing in waxed glass or preferably in hard rubber.

3. The distillation flask is heated gently at first to ensure the complete oxidation of the halogens before they can be volatilized. When the mixture begins to boil, the flask is heated strongly to distill the ruthenium; care is taken to avoid bumping. Some  $RuO_4$  (as a yellow oil) begins to distill immediately, owing to oxidation by  $NaBiO_3$ . The solution is distilled until the  $HClO_4$  begins to fume, at which point any remaining ruthenium distills. The distillation is then continued until 1 to 2 ml of  $HClO_4$  has been distilled; this requires 1 to 2 min after the fuming has begun. The receiver is then lowered, the delivery tube is rinsed with a little water, and the heat is removed.

#### PROCEDURE 1 (Continued)

4. It is necessary to keep the solution in the receiver basic during the distillation in order to avoid the loss of  $\text{RuO}_4$ . The 12 ml of 6M NaOH is sufficient to give good results with a sample containing as much as 50 millimoles of  $\text{HNO}_3$  (or HCl).
5. If the precipitation is incomplete, as indicated by a colored supernatant solution, the solution should be neutralized with conc. HCl, 1 ml of 6M NaOH should then be added, and the heating with alcohol should be repeated.
6. The filter-paper disk is washed with ethanol and ether and dried under the conditions of the procedure before weighing.
7. The precipitate of metallic ruthenium contains a small amount of oxide, and the weight is therefore about 6 per cent greater than the weight obtained by ignition in hydrogen. The ratio of the amount of observed ruthenium to the amount of true ruthenium is quite reproducible, however, and the method is satisfactory if the standardization is made under the same conditions.

#### PROCEDURE 2

##### The Determination of Fission Product Ruthenium

Source: R. P. Larsen, L. E. Ross and Gwendolyn Kesser, ANL-5810 (1957)

Transfer an aliquot containing from  $10^3$  to  $10^4$  ruthenium gamma or beta counts to a 50-ml beaker. Add 5 ml of 6 N sulfuric acid, 0.5 ml of ruthenium carrier (5 mg) and heat to fumes on a sand bath. (The loss of ruthenium from hydrochloric-nitric acid samples during this step is prevented by the prior addition of excess 12 N hydrochloric acid.) After cooling, carefully add 5 ml of water and stir. Transfer with several 6 N sulfuric acid washings to a still of the type shown in Figure 1.\* After placing the delivery arm of the still in

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\* See Fig. 4.2 of this monograph.

## PROCEDURE 2 (Continued)

the receiver, add 5 ml of 12 N sodium hydroxide to the receiver and a slurry of ice and water to the cooling bath. Slurry 0.5 g sodium bismuthate in 6 N sulfuric acid and transfer to the still with several 6 N acid rinses. Adjust the air supply to about 2 bubbles per second and distill until 5 ml of water has been distilled. Transfer the distillate to a 40-ml centrifuge cone with water and dilute to 25 ml. Add 5 ml of 95 per cent ethanol and heat to boiling. After the ruthenium is well coagulated, centrifuge for 10 minutes and pour off the supernate. Dissolve the ruthenium dioxide in 10 drops of 12 M hydrochloric acid, transfer to a 3-ml test tube with water and dilute to 2 ml. Assay for gamma activity in a well-type scintillation counter. If a beta assay is desired, the ruthenium dioxide is collected on a small filter paper, using a filter chimney assembly dried with alcohol, and mounted for counting.

## PROCEDURE 3

### Radiochemical Determination of Fission Ruthenium in Aqueous Solutions. A Nondistillation Technique

Source: R. R. Rickard and E. I. Wyatt, Anal. Chem. 31, 50 (1959)\*

## REAGENTS

Ruthenium carrier, 10 to 15 mg. per ml. Prepare by dissolving 30 grams of  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  in distilled water and diluting to 1 liter. Standardize in triplicate by pipetting 5-ml. aliquots of the stock solution into 125-ml. Erlenmeyer flasks and acidify with 10 ml. of 6 N hydrochloric acid. Heat in a hot water bath to 80° to 90° C. and add granulated magnesium slowly to reduce the ruthenium to the metal. After coagulation of the ruthenium metal, dissolve the excess magnesium by dropwise additions of concentrated hydrochloric acid. Filter the

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### PROCEDURE 3 (Continued)

ruthenium metal while hot through a tared medium-fine glass frit, wash the metal with hot distilled water, and dry with ethyl alcohol and diethyl ether washes. Desiccate the frit in a vacuum desiccator for 10 to 15 minutes, then remove the frit and weigh. The carrier yield can be expected to be between 10 and 15 mg. per ml.

Zirconium carrier, approximately 10 mg. per ml. Prepare by dissolving 35 grams of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  in 1 liter of distilled water.

#### PROCEDURE

Pipet an aliquot of a sample into a 50-ml. glass centrifuge tube, add the ruthenium carrier and 2 ml. of concentrated hydrochloric acid, and heat to boiling. Cool, and cautiously add 16 M sodium hydroxide dropwise with frequent stirring until hydrolysis of the ruthenium is evident, then 1 ml. in excess. Add 20 to 30 ml. of a saturated potassium periodate solution in distilled water and, while stirring, slowly heat to boiling over a flame. Add 1 ml. of 5% sodium hypochlorite and digest the solution at room temperature for 10 minutes. Sodium hypochlorite ensures the oxidation of any nitratonitrosyl ruthenium. The color will change from an orange to a greenish brown. Absorption spectra indicate the presence of ruthenate (5) and perruthenate (1, 8) ions.

Add 1 ml. of zirconium carrier, stir the solution thoroughly, and centrifuge. Discard the precipitate which contains most of the fission products. Decant the clear supernate into clean centrifuge tubes and add 1 ml. of zirconium carrier. Stir the solution well and centrifuge. Decant the supernate into clean centrifuge tubes, add 1 ml. of ethyl alcohol, stir, and digest in a hot water bath to coagulate the hydrated ruthenium oxides. Cool, centrifuge, and discard the supernate. Wash the precipitate with 2 M sodium hydroxide, stir, centrifuge, and discard the wash solution. Dissolve the precipitate with 2 ml. of 6 M hydrochloric acid with occasional heating over a flame. Add an equal volume of distilled water and add magnesium metal turnings slowly to reduce the ruthenium to the metal. After coagulation of the ruthenium metal, dissolve the excess magnesium with

PROCEDURE 3 (Continued)

concentrated hydrochloric acid. Centrifuge and discard the supernate. Wash the ruthenium metal with hot distilled water, centrifuge, and discard the wash solution. Dissolve the ruthenium metal with several drops of 16 M sodium hydroxide and 2 ml. of 5% sodium hypochlorite (4). Sufficient alkali is needed to prevent volatilization of ruthenium tetroxide. Heat gently over a flame and stir to obtain complete dissolution. Add 5 to 10 ml. of distilled water and 1 ml. of zirconium carrier. Stir the solution and centrifuge.

Transfer the supernatant liquid into a clean centrifuge tube and add 1 ml. of ethyl alcohol. Digest in a hot water bath to reduce and coagulate the ruthenium hydroxide. Centrifuge and discard the solution. Wash the precipitate with 2 M sodium hydroxide. Centrifuge and discard the wash solution. Dissolve the precipitate with 2 ml. of 6 M hydrochloric acid. Heat over a flame to dissolve the precipitate completely. Reduce the ruthenium to the metal by careful addition of magnesium metal. Swirl to coagulate the metal, dissolve the excess magnesium metal with concentrated hydrochloric acid, and centrifuge. Discard the liquid and wash the metal precipitate with hot distilled water. Discard the water wash solution. Collect the metal on a tared filter paper (2-cm. diameter), and wash with hot water, 95% ethyl alcohol, and diethyl ether. Weigh, mount, and count the isolated ruthenium.

References from the Source

1. Connick, R. E., Hurley, C. R., J. Am. Chem. Soc. 74, 5012 (1952).  
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4. Hopkins, B. S., "Chapters in the Chemistry of the Less Familiar Elements,"  
Vol. II, p. 23, Stipes Publishing Co., Champaign, Ill., 1939.
5. Marshall, E. D., Rickard, R. R., Anal. Chem. 22, 795 (1950).  
.....
8. Stoner, G. A., Anal. Chem. 27, 1186 (1955).

#### PROCEDURE 4

##### An Extraction Method for the Determination of Radium Ruthenium in Organic Samples

Source: D. W. Shannon, HW-48736 (1957)

#### PROCEDURE

The extractions are carried out in a 60 ml open top separatory funnel. The solutions are stirred by a motor driven centrifugal pump stirring rod. The procedure is outlined as follows:

- (1) To a 60 ml open top separatory funnel add,
  - (a) 3 ml standard organic Ru carrier, accurately measured
  - (b) Sample
  - (c) One drop of phenolphthalein.
- (2) Stir for one (1) minute.
- (3) Continue stirring and add 5 ml warm 1% NaOH.
- (4) Continue stirring for 45-60 seconds.
- (5) Continue stirring and add glacial acetic acid dropwise until the red color just disappears. Add 6-8 drops excess.
- (6) Stop stirrer and let stand for one minute while phases separate.
- (7) Draw off bottom aqueous layer only into a ruthenium distillation flask.
- (8) Repeat steps 3-7. Add each aqueous phase to the same distillation flask.
- (9) To the distillation flask: Add 2.00 ml of standard aqueous ruthenium carrier ( $\text{RuCl}_3$ ), accurately measured. Add 5 ml  $\text{H}_2\text{O}$ .
- (10) To a 50 ml glass centrifuge tube, introduce 10 ml of 6 N HCl.
- (11) When the distillation flask is in position ready to distill add:  
3-4 ml of 50 per cent  $\text{H}_5\text{IO}_6$  (periodic acid). Immediately connect the distillation flask to centrifuge tube receiver. With compressed air sparging, distill  $\text{RuO}_4$  for ten minutes.
- (12) Remove the receiver to a separate holder and add powdered Mg in small increments, with shaking after each addition, until excess Mg is present.

PROCEDURE 4 (Continued)

- (13) Place in boiling water bath, boil gently until the Ru precipitate is well coagulated. While heating, dissolve excess Mg by the dropwise addition of concentrated HCl.
- (14) Using a Hirsch funnel and suction, filter the Ru water slurry through tared No. 41 filter paper. Wash:
  - 3 times with 5 ml hot H<sub>2</sub>O
  - 3 times with 5 ml ethanol
  - 3 times with ethyl ether
- (15) Mount the ppt. and count the beta activity.

The organic carrier is prepared as follows:

- (1) To a 50 ml tube add about 2 g RuCl<sub>3</sub>, 3 ml of 6 N HCl, and 10 ml H<sub>2</sub>O.
- (2) Heat in a water bath and slowly (over 1/2 hour) add about 10 g of KNO<sub>2</sub> (potassium nitrite). Heat until the solution becomes a clear yellow-brown color.
- (3) Slowly: Add 6 N HNO<sub>3</sub> dropwise until the violent frothing subsides. Then add 2-3 ml concentrated HNO<sub>3</sub>. Heat for about 5-10 minutes. If the solution is heated too long the yield will be lowered. Solution should turn a very deep red color.
- (4) Extract about 10 times with 25 ml aliquots of TBP (tributylphosphate).
- (5) Dilute with an equal volume of SSB.
- (6) To remove water, filter through a porous paper, or allow to stand overnight then decant.
- (7) Standardize by extracting 3 ml of the carrier by the procedure above. Spike in about 10 mg accurately measured standard Ru (aqueous RuCl<sub>3</sub>). Reduce with Mg metal and weigh the precipitate. Subtract the weight of the Ru spike from the total.

## PROCEDURE 5

### The Determination of Radio-Ruthenium in Effluent and Sea Water

Source: B. A. Loveridge and A. M. Thomas, AERE C/R 2828 (1959)\*

#### B. Special reagents required (after IGO-AM/W70, ref. 12)

##### 1. Ruthenium carrier solutions:

Dissolve 0.75 grams of ruthenium trichloride in 50 ml. of water, add 5 grams of sodium hydroxide and 2 grams of potassium persulphate. Heat to boiling. When the precipitate has dissolved, add 0.5 ml. of methyl alcohol and stir thoroughly. Digest the mixture near the boiling point until the precipitate coagulates, then centrifuge the solution and discard the supernatant liquor. Wash the precipitate once with boiling water and dissolve it in 50 ml. of hot 2.5 M sodium hydroxide solution containing 2 grams of potassium persulphate. Cool and dilute to about 100 ml. Add 2 ml. of the prepared carrier solution to 5 ml. of potassium periodate - potassium hydroxide reagent (see below) in a 50 ml. standard flask and dilute to volume. Measure the optical absorbancy of this solution in 1 cm. cell at 4700Å. Dilute the ruthenium carrier solution by proportion so that the absorbancy of a 2 ml. aliquot in the alkaline periodate reagent lies between 0.6 and 0.8. Prepare a calibration chart using 0.5, 1.0, 1.5 and 2 ml. of the final ruthenium carrier solution to determine the optical absorbancy.

##### 2. Potassium periodate - potassium hydroxide reagent:

Dissolve 20 grams of potassium hydroxide and 10 grams of potassium periodate in 200 ml. of water.

\* Material is taken from this source with the permission of the authors and of the Atomic Energy Research Establishment, Harwell, nr. Didcot, Berkshire, England.

PROCEDURE 5 (Continued)

C. Details of the Method

1. To 1 liter of sample in a 1 1/2-2 liter beaker, add 10 g. potassium persulphate, 2 ml. ruthenium carrier, and 20 g of potassium hydroxide.

For smaller samples, the weight of potassium persulphate, potassium hydroxide and potassium periodate should be reduced proportionately.  
For aliquots of < 100 ml., use 1 ml. of ruthenium carrier.

Sea Water: Add 5 g. potassium periodate and heat at 90°C-95°C for 15 minutes. Stir mechanically to prevent "bumping".

Affluent: Boil for 15 minutes, then add 5 g. potassium periodate, and heat 90°C for a further 15 minutes.

The more vigorous oxidative attack on effluent is necessary for the complete recovery of radio-ruthenium.

2. Cool the solution, transfer it to a 1 liter conical separatory funnel, stir mechanically and neutralise with 16 M nitric acid until the straw colour lightens. Add 20 ml. carbon tetrachloride.

For 100 ml. aliquots add only 10 ml. carbon tetrachloride.

(In the case of sea water continue addition of nitric acid dropwise until precipitated hydroxides are dissolved)  
Add 1 ml. 16 M nitric acid in excess.  
Continue to stir vigorously for 1-2 minutes. Allow the phases to separate.  
Remove the organic phase into 50 ml. centrifuge tube.

PROCEDURE 5 (Continued)

- |   |   |
|---|---|
| 3. Add a further 10 ml. portion of carbon tetrachloride and stir vigorously for 1-2 minutes. Allow the phases to separate, then remove the organic layer into a second 50 ml. centrifuge tube. Repeat the extraction with a third 10 ml. portion of carbon tetrachloride, adding it to the second centrifuge tube. Discard the aqueous layer. | The additional portions of carbon tetrachloride are added primarily to recover residual carbon tetrachloride from the first extraction, ensuring satisfactory chemical yield. |
| 4. Wash the organic extracts by stirring with 10-15 mls. of water. Allow the phases to separate. With a dropping pipette remove and discard the bulk of the water. Centrifuge both tubes containing the organic phase and carefully combine the organic layers in a single clean <u>dry</u> 50 ml. centrifuge tube.                           | The very small residual volume of water should cling to the walls of the centrifuge tube when the organic layer is transferred.   |
| 5. To the carbon tetrachloride add 1 drop of industrial methylated spirits while swirling. Then add a further 0.5 ml. of alcohol, swirl to mix thoroughly and set the tube aside to stand until the precipitate coagulates. Centrifuge for 5 minutes and discard the supernate.   | The presence of any water will entirely prevent the separation of coagulated ruthenium dioxide, hence the importance of complete removal of the water phase in step 4.        |
| 6. Slurry the precipitated ruthenium dioxide with a few drops of anhydrous industrial methylated spirits onto an aluminum   | The aluminum absorber is used to prevent the weak beta of ruthenium <sup>106</sup> reaching   |

PROCEDURE 5 (Continued)

counting tray, using a dropping pipette the geiger counter and  
and rubber bulb. Evaporate off the necessitating back-scatter  
alcohol under an infra-red lamp then and self-absorption correction  
beta-count through an aluminum absorber for this isotope.

( $\sim 7$  mg. Al/cm<sup>2</sup>). Compare with the beta-  
activity of standards prepared from an  
<sup>106</sup>Ru-<sup>106</sup>Rh solution of known specific  
activity. (See Preparation of Reference  
Standards.)

7. Remove the precipitate of ruthenium Step 7 is the only one in the  
dioxide by tapping the bulk of the solid analysis which must be carried  
into a 50 ml. beaker. Dissolve the out strictly quantitatively  
remainder using 5 ml. of potassium and without loss.  
hydroxide/pot. periodate reagent allowing  
the reagent to flow slowly from a  
dropping pipette across the tray and  
into the beaker. Rinse the tray with  
a few drops of distilled water, allowing  
the rinsings to run into the beaker.  
Warm to complete solution if necessary  
and transfer quantitatively to a 50 ml.  
graduated standard flask and make up to  
volume. Measure the optical absorbency  
at 4700Å in a 1 cm. cell. Obtain the  
chemical yield by reference to the  
absorbancies determined for known  
aliquots of the ruthenium carrier  
solution.

PROCEDURE 5 (Continued)

Preparation of Reference Standards

1. To each of six 100 ml. samples of water, add 2 ml. ruthenium carrier solution and a suitable volume (equivalent to 0.01-0.02  $\mu\text{C}$   $^{106}\text{Ru}$ ) of a ruthenium 106 solution of known specific activity. Add 1 g. of potassium persulphate and 2 g. of potassium hydroxide. Heat to 90-95°C for 15 minutes.
- 2-3. Cool the solutions and proceed to step 2 of the method given above, using 250 ml. conical separatory funnels for the extraction with 10 + 10 + 10 ml. of carbon tetrachloride. The three portions of carbon tetrachloride are collected in the same 50 ml. centrifuge tube.
- 4-6. Follow the steps essentially as described. (Count all six samples to at least  $\pm 1\%$  precision ( $> 10,000$  counts)).
7. Dissolve only three of the ruthenium dioxide samples off the trays and determine the chemical yield of each as described in step 7. Calculate the number of microcuries of  $^{106}\text{Ru}$ - $^{106}\text{Rh}$  (counted as  $^{106}\text{Rh}$ ) on each of the three trays, average the observed activity in counts per minute and so determine the number of microcuries of ruthenium present on the untouched trays by simple proportion. Use these three remaining trays as standard references for comparison with the beta activity of sources of  $^{106}\text{Ru}$  separated from sea water and effluent.

## PROCEDURE 5 (Continued)

### References from the Source

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12. "The Determination of Radio-Ruthenium in Seaweed Ash", IGO-AM/W 70  
(February, 1957) Operations Branch, Windscale Works, U.K.A.E.A.

## PROCEDURE 6

### Low Concentrations of Ruthenium-106 in Water

Source: E. I. Wyatt and D. K. Smith, Method No. 2 21732 (R. 7-11-60),  
ORNL Master Analytical Manual; TID-7015, Sec. 2

#### I. SCOPE

This method is applicable to the determination of  $\text{Ru}^{106}$  in large volumes of water. The lower limit of measurement is about  $10^{-7}$   $\mu\text{c/ml}$ . No effort has been made to determine  $\text{Ru}^{103}$  in the presence of  $\text{Ru}^{106}$  because of low counting rates. Citrates, phosphates, oxalates, and the mineral acids do not interfere; tartrates and glucosides do interfere by forming complexes with ruthenium.

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#### V. REAGENTS

1. See Methods No. 2 0040, "Reagents," and No. 2 0041, "Radiochemical Carrier Solutions."
2. Ethyl Alcohol, 95%.
3. Ferric Nitrate Solution, approximately 50 wt %  $(\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O})$ .  
Prepare by dissolving 100 g of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in water and diluting the resulting solution to 100 ml with water.
4. Hydrochloric Acid Solution, approximately 6 M HCl. Prepare by diluting 516 ml of 11.6 M (36%) HCl to 1 liter with water.
5. Sodium Hydroxide Solution, approximately 16 M NaOH. Prepare by dissolving 672 g of NaOH in water and diluting the cooled solution to 1 liter with water.

PROCEDURE 6 (Continued)

6. Magnesium Metal, granulated.
7. Potassium Periodate, solid  $\text{KIO}_4$ .

VIII. PROCEDURE

1. Measure out two 1-liter test portions of the water samples; pour each into a separate 1500-ml beaker. Treat each test portion as follows.
2. Add about 5 ml of conc.  $\text{HCl}$ ; then stir the solution.
3. Pipet a known volume of Ru carrier into the solution.
4. Add 1 ml of  $\text{Fe}(\text{NO}_3)_3$  solution and 1 ml of zirconium holdback carrier. Heat the resulting solution almost to boiling with occasional stirring. Add 16 M  $\text{NaOH}$  until the solution has a pH of 10. To the hot basic solution add about 4 g of  $\text{KIO}_4$  and boil it for 5 min with stirring. Remove the solution from the heat source and allow the solution to cool and the precipitate to settle (NOTE a).
5. Transfer the supernatant solution to clean 1500-ml beakers; heat the solution to boiling and add about 20 ml of ethyl alcohol with stirring. Boil the solution for several minutes, remove it from the heat source, and allow the  $\text{RuO}_2$  to settle. Discard the clear supernatant solution. (If ruthenium is one of the major radioactive constituents in the starting solution, it is usually possible to omit Steps 6, 7, and 8; if so, transfer the precipitate obtained in Steps 5 to a 50-ml glass centrifuge tube and proceed with Step 9.)
6. Transfer the precipitate to a 50-ml glass centrifuge tube, add about 3 ml of water, 3 drops of 16 M  $\text{NaOH}$ , and about 2 g of  $\text{KIO}_4$ . Stir the solution; then heat it to boiling.
7. Centrifuge the mixture and decant the supernatant liquid into a new centrifuge tube. Discard the precipitate. To the supernatant liquid add 1 ml of Zr holdback carrier; stir and centrifuge the mixture.
8. Transfer the supernatant liquid to a new centrifuge tube and add to it about 5 ml of ethyl alcohol. Digest the suspension in a hot water bath in order to reduce the ruthenates and perruthenates to ruthenium dioxide. Centrifuge the mixture and discard the supernatant liquid.

## PROCEDURE 6 (Continued)

9. Wash the precipitate with hot water that has been made slightly basic with NaOH. Dissolve the precipitate in 2 ml of 6 M HCl (heat it gently if necessary).
10. Reduce the oxidized ruthenium to metallic ruthenium by the careful addition of small amounts of magnesium metal. Swirl the mixture in order to coagulate the ruthenium. Dissolve the excess magnesium with concentrated HCl; then centrifuge the suspension.
11. Discard the supernatant liquid and wash the precipitate with hot water; discard the washings.
12. Tare together a 25-mm dia watch glass and a Whatman No. 40 filter paper disk. Place the tared paper on a small Hirsch funnel; then transfer the ruthenium metal to the paper by means of washes with hot water. Filter off the water by means of suction. Wash the precipitate with three 5-ml portions of hot water, three 5-ml portions of 95% ethyl alcohol, and finally with three 5-ml portions of absolute ethyl ether.
13. Place the paper and precipitate on the watch glass in a vacuum desiccator, evacuate the desiccator for 2 min, release the suction, and evacuate it again for 5 min. Weigh the precipitate as ruthenium metal and mount it for beta counting. For the mounting and counting procedures refer to Methods No. 2 00355, "Geiger-Mueller Counter," and No. 2 0912, "Preparation of Precipitates for Counting."

### Notes

- a. Potassium periodate converts ruthenium to the ruthenate and perruthenate forms, which are soluble in caustic solutions and which will not volatilize from them.<sup>(2)</sup>

### Reference from the Source

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2. R. R. Rickard and E. I. Wyatt, "Radiochemical Determination of Fission Ruthenium in Aqueous Solutions (A Nondistillation Technique)," Anal. Chem. 31, 50 (1959).

## PROCEDURE 7

### Determination of Radioruthenium in Vegetation or Biological Materials

Source: Private communication from D. K. Smith to E. I. Wyatt

This procedure is an adaptation of Procedure 9.

The type of pretreatment required of vegetation or biological material usually depends on the type of vegetation, the bulk, the level of activity, etc. In general, all vegetation should be oven-dried to a constant weight. It may then be crushed or ground and thoroughly mixed, ashed (if the volume needs to be reduced) at a temperature of no greater than 500°C.<sup>(51)</sup> Biological material must be ashed at 500°C or less.

1. Place dry, weighed test portions of the sample in a distillation flask with a flat bottom. Add standard Ru carrier and 25 ml of 9 M  $\text{H}_2\text{SO}_4$ . Boil the mixture on a hot plate until the reaction ceases.
2. Add 1 g of  $\text{KMnO}_4$  and immediately connect to the distillation flask a condenser having an air inlet and vapor outlet. Admit air in a slow, steady stream, and submerge the vapor outlet in a 50-ml glass centrifuge tube that contains 20 ml of 6 M  $\text{NaOH}$  and that is standing in an ice bath. Heat the flask until the solution boils vigorously and brown ruthenium tetroxide vapor passes into the  $\text{NaOH}$  solution. Let the flask cool, add another gram of  $\text{KMnO}_4$  to the solution, and again boil it to distil the remaining  $\text{RuO}_4$ . Discard the contents of flask.
3. To the  $\text{NaOH}$  solution, add 3 ml of ethyl alcohol, stir the solution, and heat it in a boiling-water bath to precipitate  $\text{RuO}_2$ . Centrifuge the mixture and discard the supernatant liquid.
4. Wash the precipitate with 20 ml of boiling water that contains 1 drop of 6 M  $\text{NaOH}$ . Centrifuge the mixture, and discard the supernatant liquid.
5. Dissolve the precipitate by heating it in 2 ml of conc.  $\text{HCl}$ ; dilute the solution to 20 ml with water. Add powdered magnesium metal in small portions until black ruthenium metal precipitates. Boil the mixture to coagulate ruthenium metal; then add conc.  $\text{HCl}$  dropwise until all the magnesium metal

#### PROCEDURE 7 (Continued)

is dissolved. Boil, cool, and centrifuge the mixture; discard the supernatant liquid.

6. Take up the ruthenium metal in 5 ml of water; filter the slurry through a tared 2-cm dia filter paper (Whatman No. 40) in a Buchner funnel. Wash the metal with 20 ml of water; dry it by rinsing it with 20 ml of ethyl alcohol and 20 ml of diethyl ether.

7. Place filter paper containing the ruthenium on a watch glass, and weigh. Calculate weight of precipitate.

8. Mount the watch glass and paper on cardboard and cover them with cellophane.

9. Count the mount on the second shelf of an end-window Geiger-Mueller counter.

10. (a) Calculate counts/minute. (b) Calculate fraction of Ru carrier recovered. (c) Divide counts/minute by the fraction Ru recovered to obtain counts/minute in original solution. (d) Divide this value by the fraction of Ru leached from soil to obtain counts/minute in 10 gm sample of soil. (e) Divide by 10 to obtain counts/minute per gm of dried soil.

#### PROCEDURE 8

##### Analysis of Fission Product Mixtures

Source: E. L. Geiger, Anal. Chem. 31, 806 (1959)\*

##### A. Special Reagents

1. Leach Solution, 3 M HCl-0.1 M HF; required for insoluble filters, soil, or ashed vegetation.

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#### PROCEDURE 8 (Continued)

2. Thioacetamide Solution, 0.1 g/ml. Dissolve 10 g of thioacetamide in slightly warm distilled water. Mix the solution, allow it to cool, and then dilute it to 100 ml.

3. Ruthenium Carrier. Dissolve  $\text{RuCl}_4 \cdot 5\text{H}_2\text{O}$  in water to give a solution having a ruthenium concentration of 25 mg/ml. Not standardized.

#### B. Procedure

1. Place a test portion of the sample (or 25 ml of the leach solution) in a 50-ml erlenmeyer flask. Add 1 ml of ruthenium carrier; then adjust the volume to 35 ml with distilled water. Swirl the solution to mix them; then add 1 ml of thioacetamide solution.

2. Place the flask on a hot plate adjusted to maintain a temperature between  $90^\circ$  and  $100^\circ\text{C}$ . Do not boil the solution. Maintain this temperature until the precipitate settles to the bottom of the flask and the supernatant liquid becomes clear (~ 45 min). Filter the mixture through HA Millipore paper.

3. Place the filter paper that contains the ruthenium sulfide in a 50-ml erlenmeyer flask with the precipitate to the bottom. Add 2 or 3 ml of 8 M  $\text{HNO}_3$  to dissolve the precipitate. When the reaction is complete, place the flask on a hot plate. Boil the solution to dryness and bake the residue until fuming stops.

4. Add to the residue 3 or 4 ml of 1.5 M  $\text{HCl}$ ; evaporate the mixture to dryness. When fuming ceases, allow the flask to cool. Dissolve the residue in 25 ml of 3 M  $\text{HCl}$ -0.1 M  $\text{HF}$  solution. Add 1 ml of ruthenium carrier, adjust the volume to 35 ml with distilled water, add 1 ml of thioacetamide solution, and reprecipitate ruthenium sulfide as instructed in Step 2. Collect the precipitate for counting.

## PROCEDURE 9

### Procedures for the Analysis of Some Radionuclides Adsorbed on Soil

Source: B. Kahn, ORNL-1951 (1955)

1. Weigh duplicate 10.0 gm. samples in 125 ml distillation flasks.
2. Add 25 ml 9M sulfuric acid and approximately 20 mg. ruthenium carrier (weighed as Ru metal) and swirl to suspend soil. Heat to boiling and boil, while shaking, for 1-2 minutes. Cool in ice bath.
3. Add 1 gm. potassium permanganate and immediately connect condenser having air inlet and vapor outlet. Admit air in a slow, steady stream, and submerge vapor outlet in 50 ml glass centrifuge tube, standing in ice bath, and containing 20 ml 6M sodium hydroxide. Heat flask until solution boils vigorously and brown ruthenium tetroxide vapor passes into sodium hydroxide solution. Let cool, add another gram potassium permanganate to solution, and again boil, to distill remaining ruthenium tetroxide. Discard contents of flask.
4. To the sodium hydroxide solution, add 3 ml ethanol, stir, and heat in boiling water bath to precipitate ruthenium dioxide. Centrifuge and discard supernate.
5. Wash precipitate with 20 ml boiling water containing 1 drop sodium hydroxide. Centrifuge, and discard supernate.
6. Dissolve precipitate by heating in 2 ml concentrated hydrochloric acid and dilute to 20 ml. Add powdered magnesium metal in small portions until black ruthenium metal precipitates. Boil to coagulate ruthenium metal, then add concentrated hydrochloric acid dropwise until all magnesium metal is dissolved. Boil, cool, centrifuge and discard supernate.
7. Take up ruthenium metal in 5 ml water and filter on tared 2 cm. diameter filter paper (Whatman # 40) in Buchner funnel. Wash with 20 ml water, and dry with consecutive portions of 20 ml ethanol and 20 ml diethyl ether.
8. Place filter paper containing ruthenium on watch glass, and weigh. Calculate weight of precipitate.
9. Mount watch glass and paper on cardboard and cover with polystyrene.
10. Count on second shelf of end-window Geiger-Mueller counter.

## PROCEDURE 10

### Ruthenium Activity in Aqueous or Organic Solutions

Source: R. E. Druschel, Method No. 2 21731 (3-2-54) ORNL Master Analytical Manual; TID-7015, Sec. 2

#### I. SCOPE

This method is applicable to the determination of ruthenium activity in either aqueous or organic solutions. The ruthenium isotopes most commonly analyzed for are ruthenium-103 ( $t_{1/2} = 42$  d; ~3.7% fission yield; 0.2- and 0.7-Mev beta; 0.50-Mev gamma), and ruthenium-106 ( $t_{1/2} = 1.0$  y; 0.5% fission yield; 0.04-Mev beta; no gamma). Ruthenium-106 is the parent of rhodium-106 ( $t_{1/2} = 30$  sec; 3.5-, 3.1-, and 2.4-Mev beta; 0.51-, 0.62-, and 1.05-Mev gamma). These data are taken from publications by Hollander, Perlman, and Seaborg<sup>(2)</sup> and by Siegel.<sup>(4)</sup>

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#### V. REAGENTS

See Methods No. 2 0040, "Reagents" and 2 0041, "Radiochemical Carrier Solutions."

.....

#### VIII. PROCEDURE

1. For aqueous samples, pipet an appropriate volume (no larger than 5 ml) of the sample into the distillation flask of a ruthenium still (NOTE a) and add 2 ml of ruthenium carrier. Record the milligrams of ruthenium added. For samples that contain organic material, pipet the appropriate volume (no more than 1 ml) of sample into the distillation flask and add 2 ml of ruthenium carrier. Record the milligrams of ruthenium added. To the flask add 2 ml of ethanol and ~0.5 ml of 12 M HCl, and evaporate to dryness on a hot plate, at a low temperature. Flame the upper portion of the flask to expell any residual ethanol, cool, and add 1 ml of 16 M HNO<sub>3</sub>.

2. To the distillation flask, add 2 ml of iodine carrier, 0.5 g of NaBiO<sub>3</sub>, 1 ml of reagent-grade 85% phosphoric acid, and 10 ml of reagent-grade 78% perchloric acid. Place the condenser firmly in the flask with the outlet in a

PROCEDURE 10 (Continued)

50-ml glass centrifuge tube that contains 12 ml of 6 M NaOH. Cool the centrifuge tube in an ice bath and pass air through the system at a rate of 2-3 bubbles per second to prevent suck-backs. Heat the solution gently to boiling (NOTE b), then distill the ruthenium rapidly (avoid bumping) into 12 ml of 6 M NaOH (NOTE c).

3. Add 3 ml of ethanol to the distillate, heat it just to boiling by swirling it over a free flame, and centrifuge it (NOTE d). Suspend the precipitate in 10 ml of H<sub>2</sub>O plus 1 ml of 6 M NaOH, heat just to boiling, and centrifuge.

4. Discard the supernatant liquid and dissolve the precipitate by heating it just to boiling in 2 ml of 6 M HCl; add 10 ml of H<sub>2</sub>O. Add 0.2 g of powdered Mg metal in small portions, shaking after each addition. Continue the boiling for 2 minutes. Slowly add 5 ml of 12 M HCl to remove the excess Mg and again boil the solution for 2 minutes.

5. Filter the mixture by means of suction through a weighed Whatman No. 40 filter paper that is placed in a small Hirsch funnel. Wash the precipitate with three 5-ml volumes of hot H<sub>2</sub>O and dry it by washing it with three 5-ml volumes of 95% ethanol and with three 5-ml volumes of diethyl ether. For the mounting and counting procedures, refer to Methods Nos. 2 00355, "Geiger-Mueller Counter," and 2 0091, "Preparation of Precipitates for Counting."

Notes

- a. See Method No. 2 0010, "Apparatus, General."
- b. Heat gently at first to insure complete oxidation of halogens so that they will not be volatilized.
- c. The NaOH reagent should be free of silica.
- d. If the precipitate is incomplete, as indicated by a colored supernatant liquid, neutralize the solution with concentrated HCl, add 1 ml of 6 M NaOH, and repeat the heating with ethanol.

PROCEDURE 10 (Continued)

References from the Source

- . . . . .
2. J. M. Hollander, I. Perlman, and G. T. Seaborg, "Table of Isotopes,"  
Revs. Mod. Phys., 25, 469 (1953).
- . . . . .
4. J. M. Siegel, "Nuclei Formed in Fission: Decay Characteristics,  
Fission Yields, and Chain Relationships," J. Am. Chem. Soc., 68, 2411 (1946).

PROCEDURE 11

Analysis for Long-Lived Products in Soil

Source: N. I. Sax, J. J. Gabay, D. Revinson, B. Keisch, NYO-4604 (1954)

1. Dissolve a 100-g test portion of the soil sample in 6 M HCl. Filter off the slight residue, fuse it with a little  $\text{Na}_2\text{CO}_3$ , dissolve the melt in HCl, and add the resulting solution to the main solution. Dilute the solution to one liter in a volumetric flask.
2. Transfer an aliquot of the solution to a ruthenium distillation flask, add 10 mg of Ru carrier as  $\text{RuCl}_3$ , 5 ml of  $\text{H}_2\text{SO}_4$ , and 15 ml of 10%  $\text{NaBrO}_3$ . Place a receiving tube that contains 15 to 25 ml 2 M NaOH in an ice bath. Pass a slow stream of air continuously through the distillation flask to flush out the system. Distil until fumes of  $\text{H}_2\text{SO}_4$  appear in the distillation flask for as long as 5 minutes.
3. Transfer the contents of the receiving tube to a beaker; rinse the tube with distilled water, and transfer the rinses to the beaker. Adjust the pH of the solution to 7 with HCl, and then add 10 additional drops of HCl. Place the beaker on a hot plate and pass in  $\text{H}_2\text{O}$  for 1/2 hour.
4. Filter the mixture while it is hot, through a glass-fiber filter, mount the filter and precipitate on brass a disk, cover the disk with pliofilm, and count the mount.

## PROCEDURE 12

### Analytical Method for the Radiochemical Determination of Ruthenium 103 and 106 in Reactor Fuel Processing Plant Solutions

Source: Chief Chemist, PG Report 78 (W) (1960) \*

#### A. OUTLINE OF METHOD

##### AQUEOUS SAMPLES

Ruthenium carrier is added to the sample and the mixture is made strongly alkaline with potassium hydroxide. Potassium persulphate is added and the solution is boiled to remove reducing agents and ammonium salts, and to break down complex ruthenium compounds so that complete interchange between the carrier and the radioactive isotope is achieved. Potassium periodate is added, the solution is acidified and then extracted with carbon tetrachloride. The extract, containing the ruthenium as ruthenium tetroxide, is washed with water and the ruthenium is precipitated as ruthenium dioxide by adding methanol. The ruthenium dioxide is mounted on a stainless steel tray.

##### BUTEX AND TRIBUTYL PHOSPHATE/KEROSENE SAMPLES

The sample is stirred with a boiling alkaline solution containing ruthenium carrier. The organic phase is discarded and the aqueous extract is treated as described for aqueous samples, commencing with the addition of potassium persulphate.

##### COUNTING PROCEDURE, CHEMICAL YIELD DETERMINATION AND CALCULATION OF RESULTS

The  $\beta$  activity is counted through a  $40 \text{ mg/cm}^2$  aluminum absorber using standard GM equipment with a thin end-window tube, type EHM2 or MX 123. (This gives a total absorber, including the window and air of  $45 \text{ mg/cm}^2$ ).

The  $\gamma$  activity is counted through a lead aluminium sandwich using standard scintillation equipment.

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\* Material is taken from the source with the permission of United Kingdom Atomic Energy Authority, Development & Engineering Group, HQ, Library & Information Dept., Risley, Warrington, Lancs.

## PROCEDURE 12 (Continued)

The ruthenium dioxide, after counting, is dissolved in a mixture of potassium hydroxide and potassium periodate. The absorbancy of the solution is measured to establish the chemical yield of the separation procedure.

Ruthenium-103 is determined by comparing the gamma counting rate of the sample with those of standard sources prepared from solutions of known ruthenium-103 content counted under identical conditions. A correction is applied for the gamma activity of ruthenium-106 present in the sample source and the observed counting rate is adjusted for chemical yield.

Ruthenium-106 is determined by comparing the beta counting rate of the sample with those of standard sources prepared from solutions of known ruthenium-106 content and counted under identical conditions. The observed counting rate is adjusted for chemical yield.

### B. SPECIAL REAGENTS REQUIRED

#### 1. RUTHENIUM CARRIER SOLUTION

Dissolve 20 g of potassium periodate in a solution of 20 g of potassium hydroxide in 200 ml of water. Add 5 g of ruthenium trichloride, boil the mixture for about 2 minutes and allow the solution to cool to room temperature.

#### THE FOLLOWING PROCEDURE MUST BE CARRIED OUT IN A WELL VENTILATED FUME-HOOD

Add 25 ml of 16M nitric acid, slowly with stirring. Allow the white precipitate, due to the excess periodate, to settle for a few minutes and decant the clear yellow liquid into a one litre separating funnel. Wash the white precipitate with about 20 ml of water and add the washings to the funnel. Extract the ruthenium, as tetroxide, from the aqueous solution with three successive 100 ml portions of carbon tetrachloride, collecting the solvent in a second separating funnel. Wash the combined extracts once with 150 ml of water, transfer to a one litre bottle and add 300 ml of 8M nitric acid. Pass a stream of nitric oxide, prepared by the action of 8M nitric acid on copper metal, first through a trap to remove spray and then into one litre bottle

## PROCEDURE 12 (Continued)

through a delivery tube dipping beneath the solvent level. Pass the gas for 15 to 20 minutes frequently shaking the bottle; remove the delivery tube, shake the mixture well for one minute and transfer it to a separating funnel. Test a portion of the carbon tetrachloride layer for freedom from ruthenium, by adding a few drops of methyl alcohol - a black precipitate should not be formed - and then discard the carbon tetrachloride layer. Transfer the aqueous phase to a 600 ml beaker and boil until the volume is reduced to about 150 ml. Allow to cool and dilute the clear red solution to 750 ml with water.

Transfer 2.0 ml of the carrier solution to a 50 ml centrifuge tube. Add 40% w/v potassium hydroxide dropwise until the solution is alkaline and note the volume of reagent required. Add 5 ml of the potassium periodate/hydroxide reagent (see para. 2) boil for a few minutes and allow to cool. Transfer the solution to a graduated flask and dilute to 50 ml with water. Measure the absorbancy of the solution using a Spekker absorptiometer fitted with H503 and Ilford No. 602 filters. Correct the observed absorbancy for that of a blank on the reagents only, omitting the ruthenium carrier solution. Express the strength of the carrier solution as an absorbancy per 2 ml of carrier solution.

### 2. POTASSIUM PERIODATE/POTASSIUM HYDROXIDE MIXED REAGENT

Dissolve 50 g of analytical reagent quality potassium hydroxide and 25 g of analytical reagent quality potassium periodate in water and dilute to 500 ml.

## C. SPECIAL APPARATUS REQUIRED

### 1. $\beta$ COUNTING EQUIPMENT

Standard G.M./equipment with a thin end-window counting tube, type EEM2 or MX 123, mounted in a standard perspex sample holder type 1271 in a lead castle type 1065C.

### 2. $\gamma$ COUNTING EQUIPMENT

Standard  $\gamma$  scintillation counting equipment, type 1186A or 1386.

### 3. ALUMINIUM ABSORBERS

Thickness 40 mg/cm<sup>2</sup> aluminium.

PROCEDURE 12 (Continued)

4. LEAD/ALUMINIUM ABSORBERS

Consisting of a lead sheet, thickness  $2 \text{ g/cm}^2$  placed between two aluminium sheets, one of thickness  $0.2 \text{ g/cm}^2$  and the other  $1.75 \text{ g/cm}^2$ . The thicker aluminium is towards the source.

5. COUNTING TRAYS

Stainless steel, lipped, 1.05 inch diameter.

6. CENTRIFUGE TUBES

Pyrex, 50 ml capacity.

D. EXPERIMENTAL

If the sample portion used for analysis contains more than 1 mg of plutonium, the chemical separation treatments described below must be carried out in a glove box. Should the sample contain more than 0.1 millicuries of total beta/gamma activity, the procedures must be carried out behind adequate shielding. Samples, where the activity is below these limits, may be handled in a well ventilated fume hood.

Procedure

Notes

PRELIMINARY TREATMENT - CARRIER AND ACTIVITY INTERCHANGE

1. AQUEOUS SAMPLES

1.1. Transfer a suitable portion of the sample solution [Note (a)] to a 50 ml Pyrex centrifuge tube, washing out the pipette used with  $2M$  nitric acid and adding the washings to the tube. Add 2.0 ml of the ruthenium carrier solution.

1.2. Add 40% w/v potassium hydroxide solution, dropwise with constant shaking, until the mixture is alkaline (testing with litmus paper). Add about 1 g of

(a) 0.02-5 ml is normally a convenient volume. The portion should not contain more than 0.5 g of ammonium nitrate and the volume is also limited by the counting rate maximum of the counting equipment of about  $2 \times 10^4$  C.P.M. per sample source. If necessary, the sample solution may be previously diluted with  $2M$  nitric acid to enable an

PROCEDURE 12 (Continued)

solid potassium hydroxide and about 1 g of solid potassium persulphate. Dilute with water to about 15 ml.

aliquot, satisfying these conditions to be taken.

1.3. Stir the mixture with a mechanical stirrer and at the same time heat the centrifuge tube until the solution boils. Using litmus paper, test for the evolution of ammonia and continue boiling for about one minute after ammonium compounds, if present, have been destroyed. In the absence of ammonium compounds, boil for one minute [Note (b)].

(b) In the absence of obscuring amounts of other coloured ions or precipitates, the colour of the ruthenium solution will be seen to change from red, through a deep orange to a final characteristic greenish yellow.

2. BUTEX AND TRIBUTYL PHOSPHATE/KEROSENE SAMPLES

2.1. Transfer a suitable portion [Note (c)] of the sample solution to a 50 ml Pyrex centrifuge tube, washing out the pipette used with butex and adding the washings to the tube. Add 2.0 ml of ruthenium carrier solution.

(c) 0.1 - 5.0 ml is normally a convenient volume. This is limited by the counting rate maximum of the counting equipment of about  $2 \times 10^4$  c.p.m. per sample source. If necessary, the sample solution may be previously diluted with butex to enable an aliquot satisfying these conditions to be taken.

2.2. Add 40% w/v potassium hydroxide solution, dropwise with constant shaking, until the aqueous phase is alkaline (testing with litmus paper). Add about 1 g of solid potassium hydroxide and dilute the aqueous phase with water to about 15 ml.

## PROCEDURE 12 (Continued)

2.3. Stir the mixture with a mechanical stirrer, ensuring that the two phases are intimately mixed. At the same time, heat the centrifuge tube until the aqueous phase boils and continue boiling for about 30 seconds.

2.4. Allow to cool and centrifuge. Using a fine drawn length of glass tubing with attached rubber test, withdraw the organic phase as completely as possible and discard.

2.5. Add about 1 g of solid potassium persulphate to the aqueous phase. Stir the mixture with a mechanical stirrer and at the same time, heat the centrifuge tube until the solution boils. Boil for 2 to 3 minutes.

### 3. BUTEX AND TRIBUTYL PHOSPHATE/KEROSENE SAMPLES - ALTERNATIVE PROCEDURE

Transfer a suitable portion [Note (d)] of the sample solution to a 50 ml Pyrex centrifuge tube, washing out the pipette used with 2M nitric acid. Continue by the procedure described for aqueous samples in section 1.

(d) The sample volume must be within the range 0.02 - 0.1 ml.

### CHEMICAL SEPARATION OF RUTHENIUM

4. To the hot sample solution (see para. 1.3 or 2.5) and 5 ml of the potassium

PROCEDURE 12 (Continued)

periodate/potassium hydroxide reagent and allow the mixture to approach room temperature.

5. Add 20 ml of carbon tetrachloride. Stir the mixture mechanically ensuring intimate mixing of the two phases. Add 16M nitric acid dropwise until the aqueous phase is acid [Note (e)]. Add about 0.2 ml of the acid in excess and stir for a further 30 seconds, extracting the ruthenium as tetroxide into the carbon tetrachloride.

6. Centrifuge and allow the two phases to separate. Using a fine drawn length of glass tubing with attached rubber teat, withdraw and discard as much as possible of the aqueous phase.

7. By decantation, transfer the carbon tetrachloride phase to a clean [Note (f)] 50 ml centrifuge tube, [Note (g)].

(e) At this stage, the aqueous phase becomes markedly lighter in colour and any uranium precipitate dissolves.

(f) The tube must be free from traces of grease to avoid premature deposition of ruthenium dioxide.

(g) By careful pouring, almost complete separation of the solvent from residual amounts of the aqueous phase may be achieved, leaving only a small proportion of the solvent in the original tube.

PROCEDURE 12 (Continued)

8. Add 10 to 15 ml of water to the separated carbon tetrachloride. Stir vigorously for 20 to 30 seconds. Centrifuge and allow the phases to separate. Withdraw and discard as much as possible of the aqueous washings and decant the carbon tetrachloride to a clean centrifuge tube, taking great care to avoid contamination of the transferred solvent with aqueous phase droplets. [Note (h)].

(h) The presence of water will interfere with the subsequent separation of the precipitated ruthenium dioxide.

9. Add about 0.2 ml of methyl alcohol to the centrifuge tube. Mix by swirling the contents of the tube and allow to stand for 5 minutes. Centrifuge and allow the precipitated ruthenium dioxide to separate. Withdraw and discard the supernatant liquor.

10. Add a little acetone to the precipitate and transfer as a slurry to a stainless steel counting tray. Allow to dry. Cover the precipitate with about 10 drops of a 4 mg/ml solution of collodion in acetone and allow to dry again.

MEASUREMENT OF GAMMA ACTIVITY OF SEPARATED RUTHENIUM

11. Measure the activity on the sample counting tray using stable [Note (i)] gamma scintillation equipment.

(i) The stability of the counter may be checked statistically using a caesium-137 source counted under identical conditions.

## PROCEDURE 13

### Radiochemical Analyses Through Polarographic Methods. II. A Rapid Procedure for Technetium and Ruthenium Radionuclides in Fission Products

Source: D. L. Love, A. E. Greendale, USNRDL-TR-388 (1959)\*

#### A. Special Equipment

Polarograph and special cell (see Fig. 4.7 for details).

#### B. Procedure

1. Adjust the height of the mercury reservoir to give a drop every four seconds.
2. Evaporate a test portion of the fission-product sample to dryness in a siliconed flask or test tube. Add exactly 1 ml of a 1 M sodium citrate — 0.1 M NaOH supporting electrolyte. Transfer the mixture to a polarographic cell with a transfer pipet and float it at the desired level on CCl<sub>4</sub>. Apply 1.55 v vs. S.C.E.
3. With the aid of a stopwatch, allow the Hg drops to fall through the aqueous layer into the CCl<sub>4</sub> for exactly three minutes. The effect of drop time is shown in Fig. 4.8.
4. Drain the 3-min collection of Hg and a small amount of CCl<sub>4</sub> into a siliconed test tube. Draw off the small amount of CCl<sub>4</sub> with a vacuum tube. Wash the Hg twice with 5-ml portions of water.
5. Dissolve the mercury in exactly 1 ml of conc. HNO<sub>3</sub> (to make the gamma ray absorption by Hg a constant). Count the gamma activity of the solution in a well-type scintillation counter.

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\* Material is taken from the source with the permission of the U. S. Department of the Navy, Bureau of Ships.

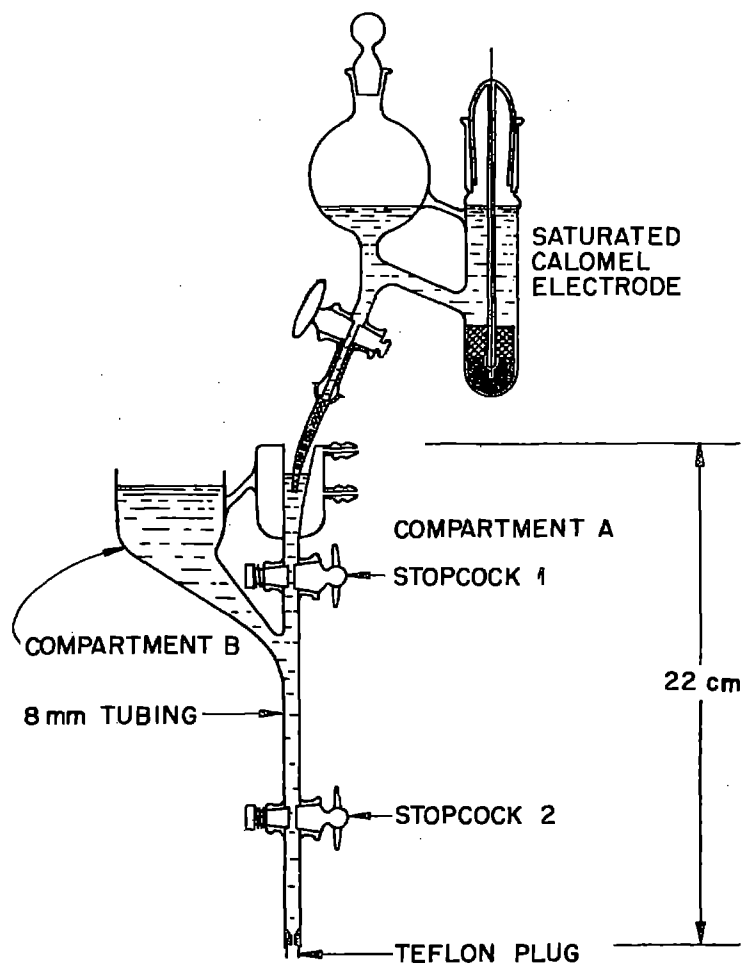


Fig. 4.7 Polarographic Cell

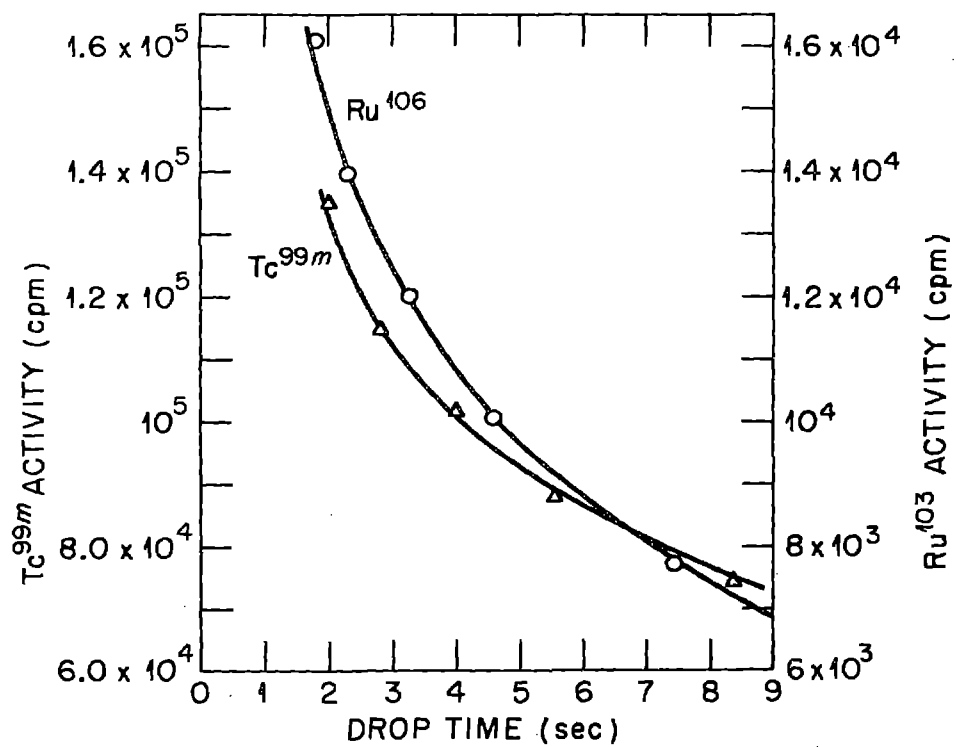


Fig. 4.8 Variation of  $Tc^{99m}$  and  $Ru^{106}$  Activities with Drop Time of the Dropping Mercury Electrode

#### PROCEDURE 14

##### An Electrolytic Method for Separating and Determining Ruthenium in Some Redox Solutions

Source: Anita Camilli, J. F. Flagg, KAPL-200 (1949)

##### A. Procedure

1. To 4 ml of 0.1 M  $\text{HNO}_3$  contained in an electrolysis cell that is fitted with a gold-plated copper electrode (see Fig. 4.9), add a test portion of the solution (aqueous or hexone) estimated to contain from 1000 to 5000 counts/min of ruthenium.
2. Add to this 25  $\mu\text{l}$  of a saturated solution of  $\text{NaNO}_2$ . Electrolyze the solution for 2.5 hr at an applied potential of 6 volts versus the platinum anode.
3. At the conclusion of the electrolysis empty the cell and wash it with four portions of water. Remove the cathode, dry it under an infrared lamp, and count the gamma.

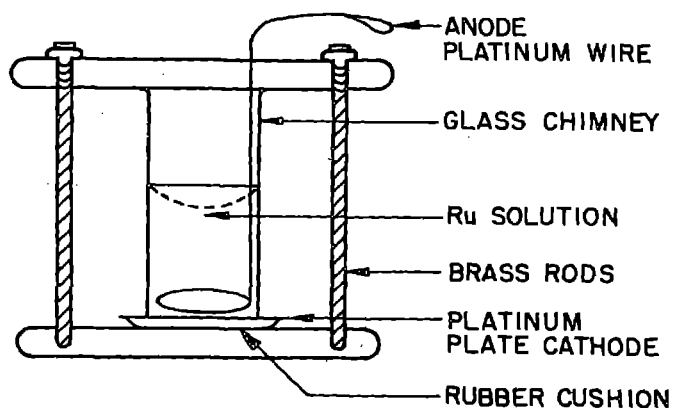


Fig. 4.9 Cell for Electrolytic Determination of Ruthenium

PROCEDURE 15

Chemical Procedures Used in Bombardment Work at Berkley

Source: W. Wayne Meinke, AECD-2738 (UCRL-432) (1949)

Element separated: Ruthenium

Procedure by: Goeckermann

Target material: ~1 g Bi metal

Time for sep'n: ~2 hr.

Type of bddt: 184" all particles

Equipment required: Distilling flask, ice, centrifuge, tubes, 110° oven

Yield: approx. 60%

Degree of purification: Decontamination factor  $> 10^4$  from fission and spallation products.

Advantages: Fair yield of pure Ru

Procedure:

1. Add 10 mg Ru and Os to aliquot of  $\text{HNO}_3$  soln of target, boil 6N  $\text{HNO}_3$  solution to volatilize  $\text{OsO}_4$ . Transfer to glass still, add 10 mg  $\text{I}^-$ , 0.5 g  $\text{NaBiO}_3$ , 1 ml concentrated  $\text{H}_3\text{PO}_4$ , and 10 ml 70%  $\text{HClO}_4$ . Boil in air stream without bumping and distill over  $\text{RuO}_4$  into 12 ml 6N  $\text{NaOH}$  in an ice bath. Distill until 1-2 ml of  $\text{HClO}_4$  have distilled (2-3 min. after fuming begins).
2. To distillate, add 3 ml  $\text{C}_2\text{H}_5\text{OH}$  and boil 1-2 min. until Ru oxide is coagulated. Wash with 10 ml  $\text{H}_2\text{O}$  and 1 ml 6N  $\text{NaOH}$  and boil.
3. Distill  $\text{RuO}_4$  again, if necessary, and reprecipitate oxide.
4. Dissolve precipitate in 2 ml hot 6N  $\text{HCl}$  and dilute to 12 ml. Add ~0.2 g Mg chips or coarse powder slowly (add aerosol) until solution passes through blue stage and  $\text{Ru}^0$  appears. Boil gently until coagulated. Add 5 ml concentrated  $\text{HCl}$  to remove excess Mg and boil, filter, wash three times with 5 ml hot  $\text{H}_2\text{O}$ , three times with 5 ml  $\text{C}_2\text{H}_5\text{OH}$ , three times with 5 ml ether, dry 10 min. at 110°C. Weigh as  $\text{Ru}^0$ .

Remarks: Some Ru may be lost from boiling a conc.  $\text{HNO}_3$  soln. Os & Tc do not ppt with the  $\text{EtOH}$ . The  $\text{NaBiO}_3$  converts I to iodate to prevent volatilization. The  $\text{H}_3\text{PO}_4$  prevents volatilization of small amounts of Mo.

## PROCEDURE 16

### Chemical Procedures Used in Bombardment Work at Berkley

Source: W. Wayne Meinke, AECD-2738 (UCRL-432) (1949)

Element separated: <u>Ruthenium</u>	Procedure by: Folger & Hicks Also by Wolfe
Target material: ~4 g. U metal	Time for sep'n: ~1 1/2-2 hr.
Type of bddt: 184" all high energy particles	Equipment required: "Ruthenium still" (all glass)

Yield: approx. 60%

Degree of purification: ~10<sup>4</sup> from all F.P. activities.

Advantages: Fairly rapid, simple procedure for obtaining a good yield of Ru.

#### Procedure:

- (1) Add 10 mg Ru and Os, boil 6 N HNO<sub>3</sub> solution to volatilize OsO<sub>4</sub>.  
Transfer to glass still, add 10 mg I<sup>-</sup>, 0.5 g NaBiO<sub>3</sub>, 5 mg Mo hold-back, 1 ml concentrated H<sub>3</sub>PO<sub>4</sub>, and 10 ml 70% HClO<sub>4</sub>. Boil in air stream without bumping and distill over RuO<sub>4</sub> into 12 ml 6 N NaOH in an ice bath. Distill until 3-4 ml of HClO<sub>4</sub> have distilled (5 min. after fuming begins).
- (2) To distillate, add 3 ml C<sub>2</sub>H<sub>5</sub>OH and boil 1-2 min. until Ru oxide is coagulated. Wash with 10 ml H<sub>2</sub>O and 1 ml 6 N NaOH and boil. (leaves Tc behind).
- (3) Distill RuO<sub>4</sub> again, if necessary, and reprecipitate oxide.
- (4) Dissolve precipitate in 2 ml hot 6 N HCl and dilute to 12 ml.  
(Take aliquot for counting here if desired). Add ~0.2 g Mg chips or coarse powder slowly (add aerosol) until solution passes through blue stage of Ru<sup>0</sup> appears. Boil gently until coagulated. Add 5 ml concentrated HCl to remove excess Mg and boil, filter, wash three times with 5 ml hot H<sub>2</sub>O, three times with 5 ml C<sub>2</sub>H<sub>5</sub>OH, three times with 5 ml ether, dry 10 min. at 110° C. Weigh as Ru<sup>0</sup>.

PROCEDURE 17

Chemical Procedures Used in Bombardment Work at Berkeley

Source: W. Wayne Meinke, AECD-2738 (UCRL-432) (1949)

Element separated: Ruthenium

Procedure by: Lindner

Target material: Sb (~.5 gm metal)

Time for sep'n: ~2 hr.

Type of bdbt: 184" D<sub>2</sub> & α

Equipment required: "Ru still"  
lusteroid tubes, centrifuge,  
cone

Yield: 50% or greater

Degree of purification: at least factor of 100

Procedure:

- (1) To dissolve the Sb metal, add 15 drops of 27 N HF to it in a lusteroid tube in a hot water bath. Add conc HNO<sub>3</sub> dropwise until dissolved (~10 min.) Dilute to ~20 ml.
- (2) To the SbF<sub>4</sub><sup>-</sup> solution add 20 mg each of Te, Sn, In, Cd, Ag, Pd, Ru, Mo and Y carriers as soluble salts. Add 2 drops conc. HCl. Centrifuge the YF<sub>3</sub> and AgCl ppts.
- (3) To half of the supn add 5 ml of 1% dimethyl glyoxime in alcohol. Centrifuge.
- (4) Place the supn on an ice bath, add 5 ml 2% α benzoin oxime and digest 2 min. Centrifuge.
- (5) Evaporate sup'n to near-dryness on hot plate. Add 10 ml H<sub>2</sub>O, 2 ml conc. H<sub>2</sub>SO<sub>4</sub> and evap to fuming for 20 min.
- (6) Transfer to "Ru distilling flask", add 5 ml 70% HClO<sub>4</sub>. Boil to fuming for 10 min, catching distillate in 5 ml 6 N NaOH.
- (7) Add 2 ml EtOH to the RuO<sub>4</sub> in NaOH, boil and centrifuge.
- (8) Dissolve the RuO<sub>2</sub> ppt in a minimum 6 N HCl.
- (9) Add 5 ml 70% HClO<sub>4</sub>. Repeat steps 6-8.
- (10) Add 0.2 gm Mg powder to aliquot of the Ru<sup>+++</sup> sol'n slowly. Boil gently to coagulate Ru.
- (11) Add 5 ml conc HCl to dissolve excess Mg and boil.
- (12) Plate the Ru metal and count.

PROCEDURE 18

Chemical Procedures Used in Bombardment Work at Berkeley

Source: W. Wayne Meinke, AECD-2738 (UCRL-432) (1949)

Element separated: <u>Ruthenium</u>	Procedure by: Newton
Target material: Thorium metal (.1-1 gm)	Time for sep'n: 1 hr.
Type of bddt: 60" alphas	Equipment required: "Ruthenium still"
Yield: $\sim 10^6$	

Procedure: The Th metal is dissolved in conc HCl plus a few drops of .2 M  $(\text{NH}_4)_2\text{SiF}_6$  to clear up the black residue. The HCl is diluted to 2 N and an aliquot taken.

- (1) Place aliquot in a distilling flask, add 20 mg Ru carrier, 10 mg  $\text{I}^-$  carrier, 0.5 gm  $\text{NaBiO}_3$ , 1 ml 85%  $\text{H}_3\text{PO}_4$  and 10 ml 70%  $\text{HClO}_4$ . Heat gently to boiling and distill Ruthenium rapidly, (avoid bumping) into 12 ml of 6 N NaOH in a 50 ml centrifuge tube in an ice bath. Distill till 1-2 ml of  $\text{HClO}_4$  have distilled (1-2 min after fuming begins).
- (2) To distillate add 5 ml EtOH. Heat gently to boiling by swirling over a flame and centrifuge. Suspend pptd Ru in 10 ml  $\text{H}_2\text{O}$  containing 1 ml of 6 M NaOH. Heat to boiling and centrifuge.
- (3) Dissolve ppt by heating to boiling in 2 ml 6 M HCl. Add 10 ml  $\text{H}_2\text{O}$ . Add 0.2 gm Mg powder in small portions, shaking with each addition. Add a few drops 0.1% aerosol to minimize frothing. Boil gently until  $\text{Ru}^0$  is well coagulated. Continue boiling 2 min. Slowly add 5 ml of 12 M HCl to remove excess magnesium and again boil 2 min.
- (4) Filter by suction on a weighed filter paper in a small Hirsch funnel. Wash three times with 5 ml hot  $\text{H}_2\text{O}$ , three times with 5 ml 95% EtOH, and three times with 5 ml  $\text{Et}_2\text{O}$ . Dry 10 min. at  $110^\circ$ . Weigh as  $\text{Ru}^0$ .

## PROCEDURE 18 (Continued)

### Remarks:

Preparation of Carrier Solution: Dissolve 28 gms commercial ruthenium chloride ( $\text{RuCl}_3\text{RuCl}_4 \times \text{H}_2\text{O}$ ) in water and dilute to 1 liter.

Standardization: Take 5 ml carrier in 250 ml erlenmeyer. Add 25 ml  $\text{H}_2\text{O}$ , 2 ml conc.  $\text{HCl}$ . Add 0.4 gms powdered magnesium metal in small portions, shaking after each addition. Add a few drops 0.1% aerosol sol to prevent frothing and boil gently till the ruthenium is coagulated and the supernate clear and colorless. Continue to boil 2 min. Add 10 ml 12 N  $\text{HCl}$  to remove excess Mg and boil 2 min. (Add more Mg if supernate not clear). Filter, wash three times with hot  $\text{H}_2\text{O}$ , three times with 5 ml portions  $\text{EtOH}$ , three times with  $\text{Et}_2\text{O}$ . Dry at  $110^\circ$  and weigh as Ru metal.

This method has been described previously (Phys. Rev. 75 17 (1949)).

## PROCEDURE 19

### Precipitation of Radoruthenium

Source: F. E. Butler, DP-494 (June 1960)

### SUMMARY

Five precipitating agents for radoruthenium were evaluated: thioacetamide, thiourea, thiophenol,  $\beta$ -mercaptanpropionic acid, and 2,3-dimercaptopropanal. The precipitates formed are classified as simple or complex sulfides. Approximately 97% recovery of  $\text{Ru}^{103}$  and  $\text{Ru}^{106}$  tracers was obtained with thioacetamide and thiourea in dilute  $\text{HCl}$  solutions, although an average recovery of 94% was obtained with all of the reagents in fission product mixtures whose normalities ranged from 5N in  $\text{HCl}$  to 6N in  $\text{NaOH}$ . Decontamination factors for other fission products and for other radioisotopes were approximately 1000. A group of eight samples can be prepared for counting in one hour.

## PROCEDURE 19 (Continued)

### EXPERIMENTAL

1. Prepare the solution to 2-3 normal in HCl. Pour 30 ml of solution into a 50<sup>ml</sup> graduated conical centrifuge tube.
2. Add 1 ml of carrier solution containing 25 mg of ruthenium (as RuCl<sub>4</sub>). Small amounts (25 mg) of hold-back carriers of Sr, Ce, Cs, Zr, or Cr may be added also, if these radionuclides are normally contained in the sample.
3. Add 2 ml of water solution containing 0.1 g/ml of either thioacetamide or thiourea.
4. Swirl the solution in the tube for thorough mixing. Place the tube in a 90 to 100°C water bath for 30 minutes.
5. Cool the solution and filter it through an "HA Millipore" filtering apparatus. Wash the brown precipitate onto the filter with a 2N HCl solution. Use tape to mount the vacuum-dried filter paper on a stainless steel disc. Count the precipitate for beta and gamma activity.

## PROCEDURE 20

### The Determination of Radio-Ruthenium in Seaweed Ash

Source: Chief Chemist, IGO-AM/W-70 (1957) \*

#### B. REAGENTS REQUIRED

##### 1. Ruthenium Carrier Solution

Dissolve 0.75 g. of ruthenium trichloride in 50 ml of water, add 5 g of sodium hydroxide and 2 g of potassium persulphate. Heat the

\* Material is taken from the source with the permission of United Kingdom Atomic Energy Authority, Development & Engineering Group, HQ, Library & Information Dept., Risley, Warrington, Lancs.

PROCEDURE 20 (Continued)

solution to boiling. When the precipitate has dissolved, add 0.5 ml of methyl alcohol and stir thoroughly. Digest the mixture near its boiling point until the precipitate coagulates, then centrifuge the solution and discard the supernatant liquor. Wash the precipitate once with boiling water and dissolve it in 50 ml of hot 2.5M sodium hydroxide containing 2 g of potassium persulphate. Cool and dilute to about 100 ml. Determine the absorbancy of a 2 ml portion as described in para. 14 of the Experimental Procedure. Dilute the carrier further if necessary so that the absorbancy of 2 ml lies between 0.6 and 0.8.

2. Potassium Periodate - Potassium Hydroxide Reagent

Dissolve 20 g of potassium hydroxide and 10 g of potassium periodate in 200 ml of water.

C. SPECIAL APPARATUS REQUIRED

1. Stainless steel crucibles, 15 ml.
2. Silica radiant heater or other infra-red heater.
3. Stainless steel counting trays, dish type. Made from discs 1.05" diameter.

D. EXPERIMENTAL

<u>Procedure</u>	<u>Notes</u>
1. Weigh 2 g of the dried sample into a small, stainless steel crucible. (Note a)	(a) The ash is prepared as described in IGO-A.M./W.35. If any carbon is present it should be removed by further heating at 500-550°C.
2. Pipette accurately 2 ml of ruthenium carrier solution into the crucible.	

PROCEDURE 20 (Continued)

3. Evaporate the solution to dryness under a radiant heater or other source of infra-red radiation. Break up the residue with a glass rod or small spatula. Add 1 g of potassium hydroxide and 4.8 g of potassium nitrate, and mix intimately with the residue.

4. Heat the crucible over a burner at (b)  $550^{\circ}\text{C}$ - $600^{\circ}\text{C}$  dull red heat (Note b) until the contents have melted, thoroughly mixing by swirling the crucible.

5. Dissolve the cooled melt by adding about 30 ml of water and 0.5 g of potassium periodate in portions. Heat to assist solution.

6. Transfer the solution to a 150 ml glass centrifuge tube (Note c) washing out the crucible with less than 5 ml of water. Add about 20 ml of Analaar or equivalent quality carbon tetrachloride. Stir mechanically so that the two phases are efficiently mixed and add 9M nitric acid dropwise until the aqueous phase is acid to litmus (Note d). Add 4-5 drops of acid in excess and stir for a further minute to extract the ruthenium tetroxide formed into the carbon tetrachloride.

(c) All the centrifuge tubes used in the analysis must be clean and free from traces of grease to avoid premature deposition of ruthenium dioxide.

(d) At this stage the aqueous phase becomes markedly lighter in colour.

PROCEDURE 20 (Continued)

7. Allow the two phases to separate and withdraw and discard as much as possible of the aqueous phase. Add 10-15 ml of water and stir the mixture for one minute. Centrifuge, draw off and discard as much as possible of the aqueous phase.

8. Pour nearly all the carbon tetrachloride solution, slowly and smoothly in one operation into a clean, dry 50 ml centrifuge tube. It will be found that any remaining aqueous phase will be left behind with the small amount of carbon tetrachloride not transferred.

(Note e)

9. Add 4-5 drops of methyl alcohol to precipitate the ruthenium dioxide, mixing the contents of the tube by swirling. Centrifuge for 5 mins. at about 2000 g (Note f) and discard the supernatant liquor.

10. Slurry with a few drops of acetone and transfer with the aid of a spitzer to a stainless steel counting tray. Allow to dry. Cover the precipitate with a few drops of a 2 mg/ml collodion solution in acetone. Allow to dry.

(e) Small amounts of water prevent the ruthenium dioxide precipitate from separating cleanly.

(f) 3000 r.p.m. in a Measuring and Scientific Equipment Co., Ltd., "Major" centrifuge.

PROCEDURE 20 (Continued)

11. Count the 106 ruthenium with a Geiger-Müller tube, through 29 mg/sq.cm. added absorber. (Note g)
- (g) The count is due to 106 rhodium, the 30 sec daughter of 106 ruthenium, which is in equilibrium with the ruthenium.  $\beta$  emission due to 106 and 103 ruthenium is absorbed by the absorber.
- 12- If the 103 ruthenium is required, count the  $\gamma$  emission with a scintillation counter and subtract from it the  $\gamma$  emission due to 106 rhodium (Note h).
- (h) The  $\gamma$  emission due to 106 rhodium is obtained by multiplying the  $\beta$  count as obtained in para. 11, by 0.375.
13. Place the counting tray in a 50 ml beaker. Add 5 ml of potassium periodate reagent. Gently swirl the liquid until the precipitate has dissolved completely.
14. Transfer the solution to a 50 ml measuring flask, dilute to the mark and mix well. Measure the absorbancy of the solution at a wave length of 470 m $\mu$  (Note i). Correct the absorbancy for any blank due to 5 ml of the reagent diluted to 50 ml.
- (i) A Unicam spectrophotometer SP.350, is a suitable instrument, using a 1 cm cell.
15. Read from a calibration graph the volume V of ruthenium carrier solution equivalent to the corrected absorbancy. Correct the observed activity (para. 11

PROCEDURE 20 (Continued)

and 12) by multiplying it by a chemical  
yield factor

$$F = \frac{2}{V}$$

16. Report as d.p.m. per gram on the  
original sample

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